An Algebraic Approach to Molecular Spectroscopy

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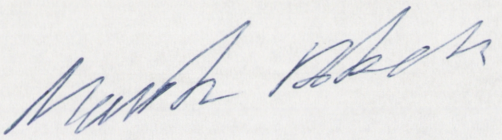
Declaration

I certify that the work contained in this thesis is my own original research, produced in collaboration with my supervisor – Dr S.Kuyucak. All material taken from other references is explicitly acknowledged as such. I also certify that the work contained in this thesis has not been submitted for any other degree.



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Abstract

This thesis gives a mean field study of the vibron model with angular momentum projection. The vibron model is a relatively new, and conceptually different model for molecular spectroscopy because it is based on spectrum generating algebras. In the applications of the vibron model, so far, dynamical symmetries have been emphasized, which provides elegant and compact solutions to the associated eigenvalue problem using the well established techniques of group theory. The alternative, symmetry breaking, approach has not been investigated in any detail presumably because it entails numerical diagonalization. Symmetry breaking is sometimes required on physical grounds and often provides a more economical and realistic description of data. Therefore, its investigation in the vibron model in some depth is be desirable.

In this thesis, it is shown that using the angular momentum projected mean field theory, one can obtain analytic solutions for various physical quantities of interest in the form of a $1/N$ expansion. The method is first applied to diatomic molecules, where analytic expressions for the energies of various vibrational bands, as well as electromagnetic transitions among them, are derived. The $1/N$ expansion results are used in a systematic study of the symmetry breaking effects, including all possible one-, two-, and three-body terms in the Hamiltonian. The formalism is then extended to triatomic molecules, and a similar study of symmetry breaking effects is performed. These investigations indicate that symmetry breaking leads to a more economical and physically more appealing description of molecular spectra, especially with regard to the moment of inertia of vibrational bands. The results obtained here clearly show the allowed ranges of parameters in a general vibron model Hamiltonian that are consistent with data, and will be very useful in more detailed numerical studies of molecules within the vibron model.

Contents

CHAPTER 1

Introduction

Algebraic techniques, and especially spectrum generating algebras (SGA), have been playing an increasingly important role in treatment of various quantum mechanical systems. The interacting boson model (IBM) [1], in particular, has made a large impact in nuclear structure studies during the last two decades. The vibron model, proposed by Iachello in 1981 [2], provides a similar algebraic framework for treating problems in molecular spectroscopy (see [3] for a comprehensive review). It has been especially useful in describing complex spectra of polyatomic molecules where traditional methods based on solving the Schrödinger equation in the coordinate space run into difficulties. The algebraic techniques developed in the nuclear case can be readily transported to the vibron model and they could also lead to a simpler description of spectroscopic data in molecules.

Group theory plays a central role in algebraic model building (see [4] for a pedagogical introduction). Perhaps the most useful aspect of group theory in this respect is the concept of dynamical symmetries. It occurs when the Hamiltonian of the system can be written in terms of the Casimir operators of a group chain. Since the Casimir operators are diagonal in the basis defined by the group chain, one only need to look up the literature for the eigenvalues of the Casimir operators to obtain an analytical expression for the energy spectrum. Group theoretical techniques can be further exploited to derive closed formulas for electromagnetic transition rates among the various eigenstates. Thus, dynamical symmetries provide elegant and compact solutions to the Schrödinger equation (in second quantized form), which otherwise would require a complicated numerical treatment. Naturally, for a dynamical symmetry to be useful, the spectrum it generates should provide, at least, a zeroth order description of some experimental spectra. This is often the case, as one can always find dynamical symmetries that can be associated with typical vibrational or rotational spectra observed in nature.

Due to their phenomenological nature, dynamical symmetries can only give an

approximate description of data and need to be refined for better correspondence with reality. This is often achieved by breaking the symmetry, that is, by including terms in the Hamiltonian which are not diagonal in the symmetry basis. If the breaking is small, its effects can be treated in perturbation theory, thus preserving the advantage of having analytical solutions. In general, though, this is not very practical, and one has to resort to numerical diagonalization. For example, most of the applications of the IBM to specific nuclear spectra have been done using numerical diagonalization. In the vibron model, an entirely different approach has been adapted. Namely, agreement with a given spectrum is improved by including higher order Casimir operators in the Hamiltonian. In this way, one preserves the dynamical symmetry and retains the advantage of analytical formulation. The rovibrational energy expression obtained this way is similar to a Dunham expansion in spirit, but with the added benefit of having eigenstates so that one can also calculate electromagnetic transitions. Iachello and collaborators have exploited this symmetry preserving approach extensively and obtained very accurate description of many molecular spectra [3].

The alternative symmetry breaking approach has been paid little attention in the past presumably because it requires numerical diagonalization of the Hamiltonian. An obvious reason for this neglect is that analytical results are superior to numerical ones, especially for purposes of systematic investigation of Hamiltonian parameters. Comparing many calculated levels to an experimental spectrum is not a very efficient method to learn about the effect of a certain parameter in a given Hamiltonian. Another, and perhaps a more pertinent reason, is that the basis space for polyatomic molecules could be too large for diagonalization.

The angular momentum projected mean field theory provides analytic solutions for general Hamiltonians in the form of a $1/N$ expansion [5]. It avoids the problems associated with numerical diagonalization while retaining the advantages of analytical formulation. Thus, it could facilitate a systematic study of symmetry breaking effects in the vibron model. The $1/N$ expansion method has previously been applied to various nuclear structure and reaction problems (see [6] for a recent review), where it played a useful role both conceptually and as a computational tool. The purpose of this thesis is to develop the $1/N$ expansion formalism for the vibron model of diatomic and triatomic molecules. The results are used in a systematic study of symmetry breaking to assess whether it provides a viable alternative to the symmetry preserving approach.

The remainder of this introduction reviews the formalism for the vibron model of diatomic molecules and its extension to polyatomic molecules, with particular

emphasis on dynamical symmetries. In the second chapter, analytic expressions are derived for energy levels and electromagnetic transitions in diatomic molecules via the $1/N$ expansion method. These results are used in a systematic investigation of symmetry breaking effects on some key spectroscopic quantities. A similar study is performed for triatomic molecules in the third chapter. Finally, the summary and conclusions are given in the last chapter.

1.1 Vibron Model for Diatomic Molecules

The basic building blocks of the vibron model are the scalar s and vector p bosons. The latter represents the dipole degree of freedom in a molecular bond while the former is needed to generate a finite, anharmonic, spectrum. For simplicity, alternate notations for the boson operators will often be used, namely

$$b_i \; i = 1,2,3,4 \;\Rightarrow\; s;\; p_m \; m = 0, \pm 1, \tag{1.1}$$

and the tensor notation

$$b_{lm} \; l = 0, m = 0; l = 1, m = 0, \pm 1 \;\Rightarrow\; s;\; p_m \; m = 0, \pm 1, \tag{1.2}$$

In the former notation, the boson operators satisfy the canonical commutation rules

$$[b_i, b_j^\dagger] = \delta_{ij}, \quad [b_i, b_j] = [b_i^\dagger, b_j^\dagger] = 0, \quad i,j = 1,2,3,4. \tag{1.3}$$

While the creation operators $b_{lm}^\dagger$ transform as spherical tensor operators, this is not true for the annihilation operators. Nevertheless, the time reversed operators, to be denoted by tilde, satisfy this requirement and will be used in the construction of physical operators

$$\tilde{b}_{lm} = (-1)^m b_{l-m}. \tag{1.4}$$

The 16 bilinear operators $\{b_i^\dagger b_j, i,j = 1,2,3,4\}$ close under the $U(4)$ algebra which forms the backbone of the vibron model. In spherical tensor notation, these can be written as

$$\hat{n}_s = [s^\dagger s]_0^{(0)} = s^\dagger s, \tag{1.5}$$

$$\hat{n}_p = = -\sqrt{3}[p^\dagger \tilde{p}]_0^{(0)} = \sum_m p_m^\dagger p_m, \tag{1.6}$$

$$\hat{L}_\mu = -\sqrt{2}[p^\dagger \tilde{p}]_\mu^{(1)}, \tag{1.7}$$

$$\hat{D}_\mu = [s^\dagger \tilde{p} + p^\dagger \tilde{s}]_\mu^{(1)}, \tag{1.8}$$

$$\hat{D}'_\mu = i[s^\dagger \tilde{p} - p^\dagger \tilde{s}]_\mu^{(1)}, \tag{1.9}$$

$$\hat{Q}_\mu = -\sqrt{2}[p^\dagger \tilde{p}]_\mu^{(1)}, \tag{1.10}$$

$$\tag{1.11}$$

The physical interpretation of these operators is as follows. The first two are the number operators for the s and p bosons, respectively. $\hat{L}_\mu$ represents the angular momentum operator of the boson system. $\hat{D}_\mu$ and $\hat{D}'_\mu$ correspond to the coordinate and momentum operators, and finally Q_μ is the quadrupole operator. Of these, the dipole operator $\hat{D}_\mu$ is of particular importance as it generates a ro-vibrational spectrum and also it is used in the description of infrared transitions.

A scalar Hamiltonian with one- and two-body terms can be easily constructed from the above operators by forming scalar products. This would lead to two one-body terms and eight two-body terms in the Hamiltonian. However, some of these interactions are redundant (i.e. they can be written in terms of the others). Further, using the boson number conservation, $\hat{n}_s + \hat{n}_p = N$, one can eliminate the $\hat{n}_s$ dependent terms from the Hamiltonian. The most general Hamiltonian with one- and two-body interactions, and with independent parameters can be written as

$$\hat{H} = \varepsilon \hat{n}_p + \sigma \hat{n}_p^2 - \kappa \hat{D} \cdot \hat{D} + \kappa' \hat{L} \cdot \hat{L}. \tag{1.12}$$

Here, ε, σ, κ, and κ' are parameters that are determined from data. A constant term is excluded from (1.12), as our main interest is in the excitation spectrum. There are various other forms of the vibron model Hamiltonian but they can all be shown to be equivalent to (1.12) up to a constant.

In general, the eigenvalue problem for the Hamiltonian (1.12) has to be solved numerically by diagonalizing it in an appropriate basis. There are codes that can do this job very efficiently [7]. However, as mentioned above, use of dynamical symmetries has been favored in literature over numerical diagonalization, therefore, this aspect of the vibron model is the focus of the following.

The $U(4)$ algebra has two rotationally invariant subalgebra chains given by

$$\begin{array}{ccccccc} U(4) & \supset & U(3) & \supset & O(3) & \supset & O(2) \quad (I) \\ | & & | & & | & & | \\ [N] & & n_p & & L & & M \end{array} \tag{1.13}$$

and

$$\begin{array}{ccccccc} U(4) & \supset & O(4) & \supset & O(3) & \supset & O(2) \quad (II). \\ | & & | & & | & & | \\ [N] & & \omega & & L & & M \end{array} \tag{1.14}$$

The quantum numbers used in the classification of states are indicated below the groups. The dynamical symmetry for the first chain, to be called $U(3)$, is obtained

when $\kappa = 0$ in the Hamiltonian (1.12). Note that $\hat{n}_p$ and $\hat{n}_p^2 + 3\hat{n}_p$ are the linear and quadratic Casimir operators of the $U(3)$ group, and $\hat{L} \cdot \hat{L}$ is that of $O(3)$. Thus the Hamiltonian consists only of the Casimir operators in the group chain as required for a dynamical symmetry. Here the p-boson number takes the values $n_p = 0, 1, \ldots, N$ and for a given n_p the angular momentum eigenvalues are given by $L = n_p, n_p - 2, \ldots, 1$ or 0. The spectrum generated by the $U(3)$ symmetry is that of a finite anharmonic oscillator with the energy formula

$$E_I = \epsilon n_p + \sigma n_p^2 + \kappa' L(L+1). \tag{1.15}$$

Since molecules behave more like rotors, it is not of much use in molecular spectroscopy, and it is not dwell on this symmetry further.

The second chain leads to the $O(4)$ dynamical symmetry. It is obtained when $\varepsilon = \sigma = 0$ in the Hamiltonian (1.12). As $\hat{D} \cdot \hat{D} + \hat{L} \cdot \hat{L}$ is the Casimir operator of the $O(4)$ group, the resulting Hamiltonian is again written solely in terms of the Casimir operators in the group chain. The $O(4)$ quantum number takes the values $\omega = N, N-2, \ldots, 1$ or 0, and for a given ω, one has $L = 0, 1, \ldots, \omega$. The $O(4)$ symmetry generates a rotor-like spectrum with the energy eigenvalues given by the formula

$$E_{II} = -\kappa\omega(\omega+2) + (\kappa + \kappa')L(L+1). \tag{1.16}$$

This may also be expressed in terms of the more familiar vibrational quantum number v through the relation

$$v = \frac{N-\omega}{2}, \tag{1.17}$$

where $v = 0, 1, \ldots, N/2$ or $(N-1)/2$, $N =$ odd or even. This shows that the boson number N is related to the maximum number of vibrational states $v_{\max}$ by

$$N = 2v_{\max} \text{ when } N = \text{even}, \quad \text{or} \quad N = 2v_{\max} + 1 \text{ when } N = \text{odd}. \tag{1.18}$$

Using Eq. (1.17), the energy formula (1.16) becomes

$$E_{II} = -\kappa\Big(N(N+2) - 4(N+1)v + 4v^2\Big) + (\kappa + \kappa')\bar{L}. \tag{1.19}$$

This spectrum is similar to that of a Morse ro-vibrator commonly used in the analysis of molecular spectra. It is obtained from the solution of the Schrödinger equation using the Morse potential

$$V(r) = V_0\left(\exp[-2a(r-r_0)] - 2\exp[-a(r-r_0)]\right). \tag{1.20}$$

Thus, the O(4) symmetry provides the required zeroth order approximation for description of molecular spectra.

In its simplest form as described above (and with a one-body dipole operator), the $O(4)$ limit corresponds to a rigid-rotor with vanishing vibrational transitions. This is not a very accurate representation of the data and needs to be improved. As noted earlier, the preferred method of refinement has been to preserve the $O(4)$ symmetry by adding higher order Casimir operators to the Hamiltonian. Since the extended Hamiltonian is still diagonal in the $O(4)$ basis, one retains the advantage of a closed expression for the energy eigenvalues, similar to Eq. (1.19) but with higher order terms. Because anharmonicity is built in the vibron model, it leads to a better representation of the data with fewer parameters compared to the traditional Dunham expansion.

The intensities of electromagnetic transitions are obtained in terms of the reduced matrix elements of the transition operator $\hat{T}$

$$T(v, L \rightarrow v', L') = |\langle N, v', J'||\hat{T}||N, v, L\rangle|^2. \tag{1.21}$$

For infrared transitions the simplest such transition operator is

$$\hat{T}^{(1)}_{\mu} = d_0 \hat{D}^{(1)}_{\mu}, \tag{1.22}$$

where d_0 is a coefficient proportional to the dipole moment of the molecule. The operator itself corresponds to a dipole function in configuration space. This operator alone does not provide a realistic description of infrared transitions. In particular, within the vibron model it does not allow transitions between different vibrational bands. As with the Hamiltonian, it may be extended to higher order terms to provide a more refined description

$$\hat{T}^{(1)}_{\mu} = d_0 \hat{D}_{\mu} + d_1(\hat{n}_p \hat{D}_{\mu} + \hat{D}_{\mu}\hat{n}_p) + d_2(\hat{n}_p^2 \hat{D}_{\mu} + \hat{D}_{\mu}\hat{n}_p^2) + \cdots. \tag{1.23}$$

In this work, only the first two terms in (1.23) are calculated, which is sufficient for description of dipole transitions among the first few vibrational bands. It will be shown in the next chapter (section 2.4) that Eq. (1.23) is not adequate for transitions involving higher-vibrational bands, and a generalization of (1.23) to an exponential form given by

$$\hat{T}^{(1)}_{\mu} = d_0 \hat{D}_{\mu} + d_1(e^{\lambda \hat{n}_p} \hat{D}_{\mu} + \hat{D}_{\mu} e^{\lambda \hat{n}_p}), \tag{1.24}$$

is necessary [8].

For Raman transitions, one needs tensor operators of rank 0 and 2. To lowest order, these are given by

$$\hat{T}^{(0)}_0 = \alpha_0 \hat{n}_p, \quad \hat{T}^{(2)}_{\mu} = \alpha_2 \hat{Q}_{\mu}, \tag{1.25}$$

where the p boson number and quadrupole operators were defined in Eqs. (1.6) and (1.11).

1.2 Extension to Polyatomic Molecules

To extend the vibron model to polyatomic molecules the boson creation and annihilation operators $b^\dagger_{\rho i}, b_{\rho i}$ are introduced for each molecular bond ρ. The index i retains its previous range. The diatomic commutation rules (1.3) are replaced by

$$[b_{\rho i}, b^\dagger_{\rho' j}] = \delta_{\rho\rho'}\delta_{ij}, \quad [b_{\rho i}, b_{\rho' j}] = [b^\dagger_{\rho i}, b^\dagger_{\rho' j}] = 0, \quad i,j = 1,2,3,4. \tag{1.26}$$

Because the different types of bosons commute, the algebraic structure obtained is the direct sum of the algebras of each degree of freedom. The total wave function is given simply by a product of individual wave functions. In terms of group representations, this is denoted by the product

$$G \equiv G_1 \otimes G_2 \otimes \ldots G_n, \tag{1.27}$$

where n is the number of bonds.

In the case of a triatomic molecule the SGA is then $U_1(4) \otimes U_2(4)$, and the basis states have the form

$$\frac{1}{\mathcal{N}} \underbrace{b^\dagger_{1i} \ldots b^\dagger_{1i'}}_{N_1} \underbrace{b^\dagger_{2j} \ldots b^\dagger_{2j'}}_{N_2} |0\rangle. \tag{1.28}$$

where $\mathcal{N}$ is a normalization, and N_1 and N_2 are the number of type-1 and 2 bosons, respectively. It is assumed that N_1 and N_2 are separately conserved. The group $U_1(4) \otimes U_2(4)$ is generated by the 32 operators $\{b^\dagger_{1i} b_{1j}, i,j = 1,2,3,4\}$ and $\{b^\dagger_{2i} b_{2j}, i,j = 1,2,3,4\}$. Each set can be written in tensor notation as in Eqs. (1.5)-(1.11), and the operators in the two sets are distinguished by by the subscript 1 or 2. In addition, one can introduce combined groups $G_{12}(n)$ whose generators are given by the sums of generators in the groups in $G_1(n)$ and $G_2(n)$. For example, the generators of $U_{12}(4)$ are given by $\{b^\dagger_{1i} b_{1j} + b^\dagger_{2i} b_{2j}, i,j = 1,2,3,4\}$.

The total Hamiltonian, which must fulfill all the constraints imposed on the $U(4)$ Hamiltonian, may be written as

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12}. \tag{1.29}$$

Here $\hat{H}_1$ and $\hat{H}_2$ include only one type of bosons and are directly obtained from the single-bond Hamiltonian (1.12). For example, H_1 is given by

$$\hat{H}_1 = \varepsilon_1 \hat{n}_{p1} + \sigma_1 \hat{n}^2_{p1} - \kappa_1 \hat{D}_1 \cdot \hat{D}_1 + \kappa'_1 \hat{L}_1 \cdot \hat{L}_1, \tag{1.30}$$

with a similar expression for H_2. $\hat{V}_{12}$ describes the interaction between the two bonds. Limited to the two-body terms, it is given by

$$\hat{V}_{12} = \sigma_{12} \hat{n}_{p1} \hat{n}_{p2} - \kappa_{12} \hat{D}_1 \cdot \hat{D}_2 + \kappa'_{12} \hat{L}_1 \cdot \hat{L}_2 + \lambda_4 M_4 + \lambda_3 M_3, \tag{1.31}$$

where M_3 and M_4 are the Majorana operators of the combined groups $U(3)$ and $U(4)$, defined by

$$M_3 = 2[p_1^\dagger p_2^\dagger]^{(1)} \cdot [\tilde{p}_2 \tilde{p}_1]^{(1)}, \tag{1.32}$$

$$M_4 = (s_1^\dagger p_2^\dagger - s_2^\dagger p_1^\dagger) \cdot (\tilde{p}_2 s_1 - \tilde{p}_1 s_2) + M_3. \tag{1.33}$$

Solution of the eigenvalue problem for a general Hamiltonian again requires numerical diagonalization, which has not been pursued in applications of the vibron model to triatomic molecules. Instead, dynamical symmetries of the $U_1(4) \otimes U_2(4)$ group have been exploited. This group has a very rich structure with many possible subgroup chains. For a complete classification, Ref. [4] may be refered to. Only the two subgroup chains that are most relevant in applications to molecular spectroscopy are considered here. In the first case, one couples the two systems at the $O(4)$ level, which leads to the so called local-mode basis

$$\begin{array}{ccccccccccc} U_1(4) & \otimes & U_2(4) & \supset & O_1(4) & \otimes & O_2(4) & \supset & O_{12}(4) & \supset & O_{12}(3) \supset O_{12}(2), \\ | & & | & & | & & | & & | & & | \quad | \\ [N_1] & & [N_2] & & (\omega_1,0) & & (\omega_2,0) & & (\tau_1,\tau_2) & & L \quad M \end{array} \quad (I) \tag{1.34}$$

while in the second case, coupling is done at the $U(4)$ level, leading to the normal-mode basis

$$\begin{array}{ccccccccccc} U_1(4) & \otimes & U_2(4) & \supset & U_{12}(4) & \supset & O_{12}(4) & \supset & O_{12}(3) & \supset & O_{12}(2). \\ | & & | & & | & & | & & | & & | \\ [N_1] & & [N_2] & & [N_1+N_2-n,n] & & (\tau_1,\tau_2)\chi & & L & & M \end{array} \quad (II) \tag{1.35}$$

The quantum numbers associated with each group are indicated below it.

For the first chain, the values of the $O(4)$ quantum numbers ω_1 and ω_2 are given as in the diatomic case. The values of (τ_1, τ_2) for a given ω_1 and ω_2 follow from

$$\tau_1 = \omega_1 + \omega_2 - \mu - \nu, \quad \tau_2 = \mu - \nu, \tag{1.36}$$

where $\mu = 0, 1, \ldots, \min(\omega_1, \omega_2)$, and $\nu = 0, 1, \ldots, \mu$. The angular momentum values L contained in a representation (τ_1, τ_2) are given by

$$\begin{aligned} L^P &= 0^+, 1^-, 2^+, \ldots, \tau_1, \quad \text{when } \tau_2 = 0, \\ L^P &= \tau_2^\pm, (\tau_2+1)^\pm, \ldots, \tau_1^\pm, \quad \text{otherwise.} \end{aligned} \tag{1.37}$$

Here the parity of levels are explicitly shown because, in contrast to the diatomic case, L is not sufficient to identify the parity of states. The symmetry Hamiltonian

for the local basis contains the Casimir operators of the $O_1(4)$, $O_2(4)$ and $O_{12}(4)$ groups, besides that of the $O_{12}(3)$. The first two are given just as in the diatomic case, and the third one follows from using the combined operators $\hat{D} = \hat{D}_1 + \hat{D}_2$ and $\hat{L} = \hat{L}_1 + \hat{L}_2$ in the definition of the Casimir operator. Denoting the strengths of the three $O(4)$ Casimir operators by A_1, A_2 and A_{12}, respectively, the energy formula in the local-mode basis is given by

$$E_I = A_1\omega_1(\omega_1+2) + A_2\omega_2(\omega_2+2) + A_{12}[\tau_1(\tau_1+2)+\tau_2^2] + BL(L+1). \quad (1.38)$$

Here the strengths A are related to those in Eqs. (1.30)-(1.31) by $\kappa_i = -A_i - A_{12}$ and $\kappa_{12} = -2A_{12}$. A more familiar expression is obtained by introducing the local vibrational quantum numbers

$$v_a = \frac{1}{2}(N_1 - \omega_1), \quad v_c = \frac{1}{2}(N_2 - \omega_2), \quad v_b = \omega_1 + \omega_2 - \tau_1, \quad l_b = \tau_2, \quad (1.39)$$

where, v_a and v_c denote local stretching vibrations and $v_b^{l_b}$, the doubly degenerate bending vibrations.

For the second chain, the $U_{12}(4)$ quantum number n is simply given by

$$n = 0, 1, \ldots, \min(N_1, N_2). \quad (1.40)$$

The reduction from $U_{12}(4)$ to $O_{12}(4)$ suffers from the multiplicity problem [3], and a third quantum number χ is required besides the $O_{12}(4)$ quantum numbers (τ_1, τ_2). Since the solution is rather complex, it is not discussed it here. The allowed angular momentum eigenvalues are as in the first chain, Eq. (1.37). Dynamical symmetry in the second chain is obtained when the Hamiltonian consists of the Casimir operators of the combined groups $U_{12}(4)$, $O_{12}(4)$, and $O_{12}(3)$. The first one is related to the Majorana operator defined in Eq. (1.33) by

$$C(U_{12}(4)) = N(N+3) - 2M_4, \quad (1.41)$$

where $N = N_1 + N_2$ is the total vibron number. Denoting the strengths of the three Casimir operators by λ_4, A_{12} and B, respectively, the energy formula in the normal-mode basis is given by

$$E_{II} = \lambda_4[(N+1)n - n^2] + A_{12}[\tau_1(\tau_1+2) + \tau_2^2] + BL(L+1). \quad (1.42)$$

Again a more familiar form follows if one uses the normal vibrational numbers defined from

$$n = v_2 + v_3, \quad \tau_1 = N - 2v_1 - v_2 - 2v_3, \quad \tau_2 = l_b, \quad (1.43)$$

where, v_1 and v_3 denote the symmetric and antisymmetric stretching vibrations and $v_2^{l_2}$, the bending vibrations.

Most molecules are closer to the spectrum generated by the local-mode Hamiltonians, hence this basis provides a reasonable starting point for further refinements of the model. (The normal-mode basis becomes useful when the masses of the three atoms are comparable.) As in the case of diatomic molecules, refinements of the model are carried out by including higher order Casimir operators in the Hamiltonian, which preserves the dynamical symmetry. Many examples of this approach are discussed in the book by Iachello and Levine [3].

The basic formalism of the vibron model reviewed in this chapter will be useful in the next chapters, where the mean field theory approach to the vibron model is developed. It forms a reference point for various physical operators (e.g. Hamiltonian, transition operators). Also, the analytical formulas obtained in the dynamical symmetry limits provide a valuable check on the accuracy of the corresponding $1/N$ expressions. More results on the $O(4)$ limit is given in Appendix A. The material presented in the thesis is partly based on the papers [9–11].

CHAPTER 2

Diatomic Molecules

In this chapter, mean field theory with angular momentum projection is developed for the vibron model of diatomic molecules. The basic ingredients of the model have been outlined in the Introduction, and are not repeated here. The first section, introduces the formulation of the mean field theory in the intrinsic frame. In the second section, angular momentum projection techniques that form the essence of this work are reviewed, and applied in some detail to the evaluation of the ground-band normalization, showing how the $1/N$ expansion follows from the projection integral. The section ends with the construction of the projected vibrational states in the lab frame. The third section contains energy calculations for the ground and first two excited vibrational bands. The variation of these expressions is also explored. The results for the electromagnetic transitions (infrared and Raman) are presented in section four. Finally, application of these results to experimental spectra is considered in section five.

Although the main focus of this thesis is to study the symmetry breaking envisaged by the Hamiltonian (1.12) with one- and two-body terms, higher-order interactions may be useful in refinements of the model. Therefore, the effect of three-body terms on the spectrum will also be considered. In general, there are eight independent three-body terms that one can write down [12]. However most of these are either constant or can be absorbed into the one- and two-body parts of the Hamiltonian. Only three of them make genuine three-body contributions to the excitation spectrum, and they can be constructed from the operators in (1.11) as

$$\hat{H}_3 = \tau_1 \hat{n}_p^3 + \tau_2(\hat{n}_p \hat{D}^2 + \hat{D}^2 \hat{n}_p) + \tau_3 \hat{n}_p \hat{L}^2, \tag{2.1}$$

where τ_i are parameters that determine the strength of the interactions. The middle term in (2.1) has been symmetrized because the two operators do not commute and $\hat{H}_3$ would not be hermitian otherwise.

2.1 Mean Field Theory

Mean field techniques have been extensively used in the vibron model to discuss its geometrical content and to provide a link with the more conventional models based on geometrical variables [12–18]. A brief review is given here, to show its uses, as well as to point out its deficiencies, which provide the motivation for improving it by incorporating angular momentum projection in the formalism.

Since the number of bosons, N, is conserved in the vibron model, the variational state used in the mean field calculations is a projective coherent state, or in more descriptive terms, a simple condensate of N intrinsic bosons. Exploiting the axial symmetry of diatomic molecules, one can choose the molecular axis along the z direction so that the variational state for the ground band of the system can be written as

$$|N,r\rangle = (N!)^{-1/2}(b^\dagger)^N|0\rangle, \quad b^\dagger = (1+r^2)^{-1/2}(s^\dagger + rp_0^\dagger). \tag{2.2}$$

Here $b^\dagger$ denotes the intrinsic boson operator and r is a variational parameter. The variable r is related to the interatomic distance in the classical limit of the vibron model ($N \to \infty$), but the functional form of this relationship appears to be exponential rather than linear [14,18]. For a given Hamiltonian $\hat{H}$, r is determined from the energy surface

$$E(r) = \langle N,r|\hat{H}|N,r\rangle, \tag{2.3}$$

by variational procedure. For the general vibron model Hamiltonian (1.12) with one- and two-body interactions, the energy surface is given by

$$E(r) = \frac{Nr^2}{1+r^2}\left[-\kappa\left(\frac{4(N-1)}{1+r^2} + \frac{3+r^2}{r^2}\right) + 2\kappa' + \varepsilon + \sigma\left(\frac{(N-1)r^2}{1+r^2} + 1\right)\right]. \tag{2.4}$$

Variation of Eq. (2.4) will be discussed in the next section after it is compared with the projected ground-band energies.

Vibrational bands, denoted by $|N,v\rangle$, can be obtained from (2.2) by replacing the intrinsic bosons b with the orthogonal fluctuation bosons b'

$$|N,v\rangle = [(N-v)!v!]^{-1/2}(b^\dagger)^{N-v}(b'^\dagger)^v|0\rangle, \quad b'^\dagger = [1+r^2]^{-1/2}(rs^\dagger - p_0^\dagger), \tag{2.5}$$

where v is the vibrational quantum number. These bands are orthogonal by construction, that is $\langle N,v|N,v'\rangle = \delta_{v,v'}$. Energy expressions for the vibrational bands follow from the expectation value of $\hat{H}$ in the states (2.5)

$$E_v = \langle N,v|\hat{H}|N,v\rangle. \tag{2.6}$$

Note that r is already fixed from the ground band, therefore it does not appear in the vibrational energies as a variable. Thus variation of the energy surface (2.3), in effect, determines the whole spectrum. The vibrational band excitation energies for the Hamiltonian (1.12) are obtained by subtracting the ground energy (2.4) from (2.6), and given by

$$E_v - E_0 = v(1+r^2)^{-2}\Big[2\kappa(N-v)\left(8r^2-(1-r^2)^2\right)+\sigma\Big(2N(2-r^2)r^2 \\ +v(r^4-4r^2+1)\Big)+(2\kappa+2\kappa'+\varepsilon)(1-r^4)\Big]. \quad (2.7)$$

One can also use the states (2.5) to discuss electromagnetic transitions among vibrational bands. For the lowest order dipole operator in (1.23), the only non-zero matrix elements are between the states v and $v' = v$, $v \pm 1$

$$\langle N, v|\hat{D}_0|N, v\rangle = (N-2v)2r/(1+r^2), \quad (2.8)$$

$$\langle N, v|\hat{D}_0|N, v+1\rangle = [(N-v)(v+1)]^{1/2}(r^2-1)/(1+r^2). \quad (2.9)$$

Note that Eq. (2.9) vanishes in the O(4) limit ($r = 1$) but not in general. This provides a first glimpse of how breaking of the O(4) symmetry may lead to an improved agreement with data.

2.2 Angular Momentum Projection

Because the condensate states (2.5) break the rotational invariance, matrix elements obtained in the intrinsic frame are correct to leading order in $1/N$ [5]. Hence the mean field theory provides only an approximate solution, suitable for a qualitative description of spectroscopic quantities. For comparison with experimental data, one needs more accurate results, which can be achieved by performing angular momentum projection before variation. Since variation after projection (VAP) with a complete set of states is equivalent to solving the Schrödinger equation, this approach can provide analytical solutions for general vibron model Hamiltonians. Such a program has been carried out in the IBM [5] and was shown to lead to a $1/N$ expansion for all matrix elements.

Angular momentum projection from a general intrinsic state is rather complicated and usually requires a large numerical effort [19]. The situation is considerably simplified if the system has axial symmetry. Then the intrinsic states have well-defined quantum numbers K for projection on to the body-fixed axis, and the expectation value of a Hamiltonian in an intrinsic state ϕ_K is given by

$$E(L) = \langle\phi_K|HP^L_{KK}|\phi\rangle/\langle\phi|P^L_{KK}|\phi_K\rangle, \quad (2.10)$$

where P^L_{MK} is the projection operator defined as [20]

$$P^L_{MK} = \frac{2L+1}{8\pi^2} \int D^{L*}_{MK}(\Omega) R(\Omega) d\Omega. \tag{2.11}$$

In (2.11), $R(\Omega)$ is the rotation operator which rotates the system through the three Euler angles (α, β, γ), collectively denoted by Ω, and D^L_{MK} is a Wigner D-function. Note that in Eq. (2.10), the expectation value is divided by the normalization because, contrary to (2.3), the projected states are not normalized. Since all the intrinsic states (2.5) have $K = 0$, the α and γ integrals in Eq. (2.11) simply give 2π each, and the projection operator takes a particularly simple form

$$P^L_{00} = \frac{2L+1}{2} \int_0^\pi d\beta \sin\beta P_L(\cos\beta) e^{-i\beta \hat{L}_y}. \tag{2.12}$$

Here $D^{L*}_{00}(\Omega) = P_L(\cos\beta)$ is used, which is a Legendre function, and $\hat{L}_y$ is the y component of the angular momentum operator $\hat{L}$.

2.2.1 Normalization Integral

As an illustration of how the $1/N$ expansion follows from angular momentum projection, the normalization $\mathcal{N}(N, L)$ for the condensate (2.2)is evaluated in some detail. As will be seen later, all the matrix elements can be reduced to expressions containing $\mathcal{N}(N, L)$, therefore their accuracy depends directly on how accurately $\mathcal{N}(N, L)$ is evaluated. Besides the key role it plays in the formulation of the method, $\mathcal{N}(N, L)$ also serves as a simple example to demonstrate the boson calculus and angular momentum algebra techniques, which are extensively used in the $1/N$ expansion calculations.

The spherical tensor notation for the boson operators introduced in Eq. (1.2) provides a more compact representation of the intrinsic boson operator (2.2), given by

$$b^\dagger = \sum_l x_l b^\dagger_{l0}, \tag{2.13}$$

where the normalized mean fields x_0 and x_1 are related to that of r in (2.2) by

$$x_0 = 1/(1+r^2)^{1/2}, \quad x_1 = r/(1+r^2)^{1/2}. \tag{2.14}$$

Besides being compact, this notation is sometimes more advantageous in handling complex angular momentum algebra operations. Thus, in the following, either notation for the intrinsic boson operators will be used, depending on their suitability.

From Eq. (2.12), $\mathcal{N}(N, L)$ is defined as

$$\begin{aligned} \mathcal{N}(N, L) &= \langle N, r | P^L_{00} | N, r \rangle, \\ &= \frac{2L+1}{2N!} \int_0^\pi d\beta \sin\beta \, P_L(\cos\beta) \langle 0 | b^N e^{-i\beta \hat{L}_y} (b^\dagger)^N | 0 \rangle. \end{aligned} \tag{2.15}$$

The first step is to apply rotation operator to the condensate. Writing the condensate explicitly as a product and inserting the identity operator $I = e^{-i\beta\hat{L}_y} e^{i\beta\hat{L}_y}$ in between each product, it is clear that rotating the condensate is equivalent to a condensate of rotated intrinsic bosons $b_R^\dagger$ defined as

$$b_R^\dagger = e^{-i\beta\hat{L}_y}\, b^\dagger\, e^{i\beta\hat{L}_y}. \tag{2.16}$$

Using the well-known formula for the rotation of spherical tensors [20], we obtain from (2.16)

$$b_R^\dagger = (1+r^2)^{-1/2}\Big(s^\dagger + r\sum_m d^1_{m0}(\beta) p_m^\dagger\Big), \tag{2.17}$$

where d^1_{m0} is a Wigner d-function. The next step is to evaluate the matrix element in Eq. (2.15). The standard technique is to commute all the annihilation operators to the right, which could be cumbersome especially in cases involving many different (but not commuting) boson operators. Schwinger's boson calculus [21], where one replaces the annihilation operators by differentials acting on the creation operators (or vice-versa), offers a much simpler method for this purpose. Thus the matrix element in (2.15) can be written as

$$\langle 0|b^N (b_R^\dagger)^N|0\rangle = \langle 0|(\partial/\partial b^\dagger)^N (b_R^\dagger)^N|0\rangle = N!\langle 0|(\partial b_R^\dagger/\partial b^\dagger)^N|0\rangle. \tag{2.18}$$

The last derivative corresponds to a simple contraction of two boson operators, e.g., for $b = \sum_i x_i b_i$, $b' = \sum_j x'_j b_j$, it is given by

$$\langle 0|bb'^\dagger|0\rangle = \langle 0|\partial b'^\dagger/\partial b^\dagger|0\rangle = \langle 0|\sum_{ij} x_i x'_j(\partial b_j^\dagger/\partial b_i^\dagger)|0\rangle = \sum_{ij} x_i x'_j \delta_{ij} = \sum_i x_i x'_i. \tag{2.19}$$

Using this result in Eqs. (2.17) and (2.18), the matrix element may be written

$$\langle 0|b^N (b_R^\dagger)^N|0\rangle = N!\Big[\frac{1+r^2\cos\beta}{1+r^2}\Big]^N \equiv N![Z(\beta)]^N. \tag{2.20}$$

Substituting Eq. (2.20) in (2.15), yields the following integral for the normalization

$$\mathcal{N}(N,L) = \frac{2L+1}{2}\int_0^\pi d\beta \sin\beta\, P_L(\cos\beta)[Z(\beta)]^N. \tag{2.21}$$

After the transformation $z = \cos\beta$, the integral in (2.21) takes the form

$$\mathcal{N}(N,L) = \frac{2L+1}{2(1+r^2)^N}\int_{-1}^1 dz\, P_L(z)[1+r^2 z]^N. \tag{2.22}$$

Eqs. (2.21-2.22) are the key integrals that control the accuracy of the $1/N$ expansion formulas. In the original papers where the $1/N$ expansion formalism was developed for the IBM [5], a Gaussian approximation was used for the corresponding

$[Z]^N$, which limited the accuracy of the formulas to order $1/N$. Later, by exploiting the symmetries of the boson system [6], it was evaluated to higher orders in $1/N$. While the integral in (2.22) looks deceptively simple, it is not available in standard tables, and only recently has it been evaluated in closed form in terms of the hypergeometric function ${}_2F_1$ [22]. (In Appendix B, another evaluation, based on the improvement of the Gaussian approximation, is given. The reason being that this method can be generalized to polyatomic case while the others cannot.) Ref. [22] contains details of the direct integration and only the final result here is quoted here

$$\mathcal{N}(N,L) = \left(\frac{2L+1}{N+1}\right)\left(\frac{1+r^2}{2r^2}\right)\Big[{}_2F_1(-L,L+1;N+2;(1+r^2)/2r^2) \\ -(-1)^L\left(\frac{1-r^2}{1+r^2}\right)^{N+1}{}_2F_1(-L,L+1;N+2;(-1+r^2)/2r^2)\Big]. \quad (2.23)$$

Here the first term arises from the integral range $[1,0]$ and the second one from $[0,-1]$. For identical parity boson systems, the second term would be equal to the first one, leading to a factor of 2. For the mixed parity *sp*-boson system, the second term is clearly much smaller than the first one, suppressed by the exponential factor in front. In fact, it vanishes in the O(4) limit when $r = 1$, and it is completely negligible for realistic breaking of the O(4) limit when r is near 1 (in a typical case with $r = 1.2$, $N = 40$, the suppression factor is 10^{-30}). Therefore, in the following, the contributions from the second term are ignored to simplify the expressions.

To make further progress, first note that the quantity "a" defined as

$$a = 2r^2/(1+r^2), \quad (2.24)$$

provides a more convenient parametrization for $\mathcal{N}(N,L)$. Since the mapping is one-to-one ($[0,\infty]$ is mapped onto $[0,2]$) and monotonous, it will have no effect on the variational problem. This choice for "a" is preferred over its inverse, because physically it corresponds to the "average angular momentum squared" carried by an intrinsic boson. To bring $\mathcal{N}(N,L)$ into a standard form, the hypergeometric function in (2.23) is written explicitly as

$${}_2F_1(-L,L+1;N+2;x) = 1 - \frac{\bar{L}}{N+2}x + \frac{\bar{L}(\bar{L}-2)}{2(N+2)(N+3)}x^2 \\ -\frac{\bar{L}(\bar{L}-2)(\bar{L}-6)}{3!(N+2)(N+3)(N+4)}x^3 + \cdots, \quad (2.25)$$

Here the bar denotes the angular momentum eigenvalues, $\bar{L} \equiv L(L+1)$. Since projection involves $\bar{L}$ rather than L, this compact notation is used throughout the paper. Expanding Eq. (2.25) in $1/N$ and $\bar{L}$, finally yields the desired $1/N$ expansion

for the normalization

$$\mathcal{N}(N,L) = \frac{2L+1}{aN}\Big[1 - \frac{1}{aN}\left(\bar{L}+a\right) + \frac{1}{2(aN)^2}\left(\bar{L}^2 + (6a-2)\bar{L} + 2a^2\right) - \frac{1}{3!(aN)^3}\left(\bar{L}^3 + (18a-8)\bar{L}^2 + (42a^2 - 36a + 12)\bar{L} + 6a^3\right) + \ldots\Big] \quad (2.26)$$

Note that the expansion is in fact in the product aN, which corresponds to the "average angular momentum squared" of the condensate [23]. While it may seem more appealing to use $L_c = aN$ rather than N itself as the expansion parameter, this is not done because N is a fixed number whereas "a" is a variational parameter dependent on the choice of the Hamiltonian.

For future notational convenience, a reduced normalization function $F(N,L) = \mathcal{N}(N,L)/(2L+1)$ is introduced, and Eq. (2.26) rewritten in a compact form

$$F(N,L) = \frac{1}{aN}\sum_{n=0}\frac{(-1)^n}{n!(aN)^n}\sum_{m=0}^{n}\alpha_{nm}\bar{L}^m. \quad (2.27)$$

As is seen from Eq. (2.26), the coefficients α_{nm} are polynomials in "a". A complete list to order $1/N^6$ is given in below in a layer format. Layers are defined such that α_{nm} with $n-m+1=k$ belongs to the k'th layer, that is α_{nn} forms the first layer, α_{nn-1} second, etc. The significance of the concept of layers will become apparent in the next section where matrix elements are evaluated using the $1/N$ expansion

$$\begin{aligned}
\text{1st layer} &: \alpha_{nn} = 1,\\
\text{2nd layer} &: \alpha_{10} = a, \quad \alpha_{21} = 6a-2, \quad \alpha_{32} = 18a-8,\\
&\quad \alpha_{43} = 20(2a-1), \quad \alpha_{54} = 75a-40, \quad \alpha_{65} = 14(9a-5),\\
\text{3rd layer} &: \alpha_{20} = 2a^2, \quad \alpha_{31} = 6(7a^2-6a+2), \quad \alpha_{42} = 4(75a^2-80a+27),\\
&\quad \alpha_{53} = 4(325a^2-375a+127), \quad \alpha_{64} = 28(150a^2-180a+61),\\
\text{4th layer} &: \alpha_{30} = 6a^3, \quad \alpha_{41} = 24(15a^3-25a^2+20a-6),\\
&\quad \alpha_{52} = 4(1350a^3-2600a^2+2025a-576),\\
&\quad \alpha_{63} = 24(1750a^3-3500a^2+2667a-731),\\
\text{5th layer} &: \alpha_{40} = 24a^4, \quad \alpha_{51} = 120(31a^4-90a^3+130a^2-90a+24),\\
&\quad \alpha_{62} = 24(4515a^4-14000a^3+18900a^2-12096a+3000),\\
\text{6th layer} &: \alpha_{50} = 120a^5,\\
&\quad \alpha_{61} = 720(63a^5-301a^4+700a^3-840a^2+504a-120).
\end{aligned} \quad (2.28)$$

Finally, note that the second term in Eq. (2.23) leads to an identical expansion in $1/N$ and $\bar{L}$. Thus, should the need arise, it could be easily included in the final result by modifying the coefficients α_{nm}.

2.2.2 Construction of Projected States

The condensate (2.2), with the VAP procedure, provides an exact description of the ground-band ($v = 0$) states. The same thing is not true for the vibrational bands (2.5) defined in the intrinsic frame. First, although they are orthogonal by construction, this property is lost after angular momentum projection. Secondly, comparison with the exact form of the states in the O(4) limit (see Eq. (A.7) in Appendix A) shows that there are extra pieces involved. The O(4) limit is used as a guide in constructing a new set of vibrational states in the intrinsic frame, which remain orthogonal after projection. Inspecting the O(4) intrinsic states in Eq. (A.7) suggests the form

$$
\begin{aligned}
|N, v = 1\rangle &= [(N-1)!]^{-1/2} \left[b^\dagger b'^\dagger + \xi_1 p_1^\dagger p_{-1}^\dagger\right] (b^\dagger)^{N-2}|0\rangle, \\
|N, v = 2\rangle &= [2!(N-2)!]^{-1/2} \left[(b^\dagger)^2 (b'^\dagger)^2 - 2\xi_2 b^\dagger b'^\dagger p_1^\dagger p_{-1}^\dagger + \xi_2' (p_1^\dagger p_{-1}^\dagger)^2\right] (b^\dagger)^{N-4}|0\rangle.
\end{aligned}
\tag{2.29}
$$

Only the first two vibrational bands are considered in this work, but it should be obvious from these examples how to construct intrinsic states for higher vibrational bands. In Eq. (2.29), the coefficients ξ are determined from orthogonality conditions with the lower vibrational bands. For example, orthogonality of the $v = 0$ and $v = 1$ bands requires

$$
\langle N, v = 1 | P_{00}^L | N, v = 0\rangle = 0. \tag{2.30}
$$

To evaluate this matrix element, one needs the following boson operator derivatives, which will recur throughout the excited band calculations

$$
\begin{aligned}
\left(\frac{\partial b_R'^\dagger}{\partial b^\dagger}\right) &= \sum_{ll'm} x_l x_{l'}' d_{m0}^{l'}(\beta) \frac{\partial b_{l'm}^\dagger}{\partial b_{l0}^\dagger}, \\
&= \sum_{lm} x_l x_l' d_{m0}^{l}(\beta), \\
&= \left(\frac{\partial b_R^\dagger}{\partial b'^\dagger}\right), \\
&= Y(\beta)
\end{aligned}
\tag{2.31}
$$

$$
\begin{aligned}
\left(\frac{\partial b_R'^\dagger}{\partial b'^\dagger}\right) &= \sum_{ll'm} x_l' x_{l'}' d_{m0}^{l'}(\beta) \frac{\partial b_{l'm}^\dagger}{\partial b_{l0}^\dagger}, \\
&= \sum_{lm} x_l'^2 d_{m0}^{l}(\beta), \\
&= Z'(\beta)
\end{aligned}
\tag{2.32}
$$

$$
\begin{aligned}
\left(\frac{\partial b_R^\dagger}{\partial p_{\pm1}^\dagger}\right) &= \sum_{lm} x_l d_{m0}^{l'}(\beta) \frac{\partial b_{lm}^\dagger}{\partial b_{1\pm1}^\dagger}, \\
&= x_1 d_{\pm10}^{1}(\beta).
\end{aligned}
\tag{2.33}
$$

Here, x_l' denote the mean fields orthogonal to x_l. Using these derivatives, the intrinsic matrix element in Eq. (2.30) can be expressed as

$$\langle N, v=1|e^{-i\beta\hat{L}_y}|N, v=0\rangle = \sqrt{N}\left[Y(\beta)Z^{N-1}(\beta) + \xi_1 x_1^2 d^1_{10}(\beta)d^1_{-10}(\beta)Z^{N-2}(\beta)\right], \tag{2.34}$$

which translates to the condition

$$\int_0^\pi d\beta \sin\beta\, d^L_{00}\left[[Z(\beta)]^{N-1} r(1-d^1_{00}) + \xi_1[Z(\beta)]^{N-1} r^2 d^1_{10} d^1_{-10}\right] = 0, \tag{2.35}$$

where $Z(\beta)$ is defined in Eq. (2.20). Using Eq. (D.1), one can couple the various d-functions in (2.35), to a single function d^J_{00}. The resulting β integral has the same form as the normalization integral in (2.21), hence the condition (2.35) can be written as

$$\sum_J\left[\sum_{l=0}^{1}(-1)^l F(N-1,J) + \xi_1 r \sum_l \langle 11\, 1-1|l0\rangle\langle 10\, 10|l0\rangle F(N-2,J)\right]\langle L0\, l0|J0\rangle^2 = 0. \tag{2.36}$$

Appendix D contains the bais for evaluation of the angular momentum sums over the Clebsch-Gordan (C-G) coefficients in Eq. (2.36). Both these sums and the division in (2.36) can be carried out most efficiently using the Mathematica software [24]. The resulting expression for ξ_1 to order $1/N^5$ is given by

$$\begin{aligned}\xi_1 = \left(\frac{2-a}{a}\right)^{1/2}\Bigg\{&1 + \frac{2(1-a)}{aN}\sum_{m=0}\left(\frac{2-a}{aN}\right)^m \\ &-\frac{\bar{L}}{(aN)^2}2(1-a)\left[(1+\frac{7-5a}{aN}+\frac{3(2-a)(6-5a)}{(aN)^2}\right. \\ &\qquad\left.+\frac{176-336a+201a^2-37a^3}{(aN)^3}\right] \\ &-\frac{\bar{L}^2}{(aN)^3}(1-a)\left[1+\frac{2}{aN}-\frac{3(12-24a+11a^2)}{(aN)^2}\right] \\ &-\frac{\bar{L}^3}{(aN)^4}(1-a)\left[1+\frac{2(2-a)}{aN}\right] \\ &-\frac{\bar{L}^4}{(aN)^5}(1-a)\Bigg\}.\end{aligned} \tag{2.37}$$

where $r = [a/(2-a)]^{1/2}$ from Eq. (2.24) has been substituted.

Orthogonality of the $v=2$ band to the $v=0$ and 1 bands requires

$$\langle N, v=2|P^L_{00}|N, v=0\rangle = 0, \quad \langle N, v=2|P^L_{00}|N, v=1\rangle = 0. \tag{2.38}$$

Following steps similar to above, the two conditions in (2.38) can be converted to two linear equations in the unknowns ξ_2 and ξ_2'. The first condition is

$$\langle N, v=2|P^L_{00}|N, v=0\rangle \;=\; \sum_J\sum_{l=0}^{4}\Big[2(2\delta_{l0}-3\delta_{l1}+\delta_{l2})F(N-2,J)$$

$$+\xi_2 r(\delta_{l0} - \frac{3}{5}\delta_{l1} - \delta_{l2} + \frac{3}{5}\delta_{l3})F(N-3,J)$$
$$+\xi_2' r^2(\frac{2}{5}\delta_{l0} - \frac{4}{7}\delta_{l2} + \frac{6}{35}\delta_{l4})F(N-4,J)\Big]\langle L0l0|J0\rangle^2 = 0, \quad (2.39)$$

and the second is

$$\begin{aligned}
\langle N, v=2|P_{00}^L|N, v=1\rangle \;=\; & \sum_J \sum_{l=0}^{6}\Big\{ \\
& (N-1)r\Big[6930(1+r^2)\left((3r^2-1)\delta_{J0} + 3(1+r^2)\delta_{J1} - 2\delta_{J2}\right)F(N-2,J) \\
& +4158(N-2)r^2\left(5\delta_{J0} - 9\delta_{J1} + 5\delta_{J2} - \delta_{J3}\right)F(N-3,J) \\
& +693\xi_2 r(1+r^2)\left(5(2-r^2)\delta_{J0} - 9\delta_{J1} - 5(2-r^2)\delta_{J2} + \delta_{J3}\right)F(N-3,J) \\
& +594\xi_2(N-3)r\left(-7\delta_{J0} + 7\delta_{J1} + 5\delta_{J2} - 7\delta_{J3} + 2\delta_{J4}\right)F(N-4,J) \\
& -792\xi_2' r^2(1+r^2)\left(7\delta_{J0} - 10\delta_{J2} + 3\delta_{J4}\right)F(N-4,J) \\
& +66\xi_2'(N-4)r^4(21\delta_{J0} - 9\delta_{J1} - 30\delta_{J2} + 14\delta_{J3} + 9\delta_{J4} - 5\delta_{J5})F(N-5,J)\Big] \\
& +\xi_1\Big[6930(1+r^2)^2\left(-\delta_{J0} + \delta_{J2}\right)F(N-2,J) \\
& +2772(N-2)r^2(1+r^2)\left(5\delta_{J0} - 3\delta_{J1} - 5\delta_{J2} + 3\delta_{J3}\right)F(N-3,J) \\
& +594(N-2)(N-3)r^4\left(-7\delta_{J0} + 7\delta_{J1} + 5\delta_{J2} - 7\delta_{J3} + 2\delta_{J4}\right)F(N-4,J) \\
& +693\xi_2 r(1+r^2)^2\left(10\delta_{J0} - 6\delta_{J1} + 5\delta_{J2} - 9\delta_{J3}\right)F(N-3,J) \\
& -198\xi_2(N-3)r^3(1+r^2)\left(7\delta_{J0} + 21\delta_{J1} - 25\delta_{J2} - 21\delta_{J3} + 18\delta_{J4}\right) \\
& \qquad \times F(N-4,J) \\
& +66\xi_2(N-3)(N-4)r^5\left(21\delta_{J0} - 9\delta_{J1} - 30\delta_{J2} + 14\delta_{J3} + 9\delta_{J4} - 5\delta_{J5}\right) \\
& \qquad \times F(N-5,J) \\
& +396\xi_2' r^2(1+r^2)^2\left(-14\delta_{J0} + 5\delta_{J2} + 9\delta_{J4}\right)F(N-4,J) \\
& +264\xi_2'(N4)r^4(1+r^2)\left(9\delta_{J1} - 14\delta_{J3} + 5\delta_{J5}\right)F(N-5,J) \\
& +18\xi_2'(N-4)(N-5)r^6\left(-33\delta_{J0} + 55\delta_{J2} - 27\delta_{J4} + 5\delta_{J6}\right)F(N-6,J)\Big]\Big\} \\
& \times\langle L0l0|J0\rangle^2 \\
& \qquad = \; 0. \qquad (2.40)
\end{aligned}$$

These, in turn, can be solved for each power of $\bar{L}$ and $1/N$, leading to the expressions (to order $1/N^4$)

$$\xi_2 = \left(\frac{2-a}{a}\right)^{1/2}\Big\{1 + \frac{2(1-a)}{aN}\sum_{m=0}\left(\frac{4-a}{aN}\right)^m$$
$$-\frac{\bar{L}}{(aN)^2}2(1-a)\Big[(1 + \frac{11-5a}{aN} + \frac{3(34-32a+7a^2)}{(aN)^2}\Big]$$

$$-\frac{\bar{L}^2}{(aN)^3}(1-a)\Big[1+\frac{8}{aN}\Big]-\frac{\bar{L}^3}{(aN)^4}(1-a)\Big\},$$

$$\xi_2'=\Big(\frac{2-a}{a}\Big)\Big\{1+\frac{4(1-a)}{aN}\sum_{m=0}\Big(\frac{4-a}{aN}\Big)^m$$
$$-\frac{\bar{L}}{(aN)^2}4(1-a)\Big[(1+\frac{11-5a}{aN}+\frac{3(4-a)(8-5a)}{(aN)^2}\Big]$$
$$-\frac{\bar{L}^2}{(aN)^3}2(1-a)\Big[1+\frac{2+6a}{aN}\Big]-\frac{\bar{L}^3}{(aN)^4}2(1-a)\Big\}. \qquad (2.41)$$

The O(4) limit ($r=a=1$), provides a useful check against any errors in the calculations. For $a=1$, all the coefficients ξ in Eqs. (2.37) and (2.41) reduce to 1 in agreement with the group theoretical result given in Eq. (A.7).

As in the case of the ground band, the vibrational intrinsic states (2.29) need to be normalized in the lab frame. The normalization for the state $|N,v\rangle$ is defined as

$$\mathcal{N}(N,v,L)=\langle N,v|P^L_{00}|N,v\rangle. \qquad (2.42)$$

Evaluation of these matrix elements is similar to the cases discussed above but they are much longer due to the extra terms (e.g., for $v=1$, there are 7 distinct terms in the normalization). Therefore, only some of the steps are given below for the $v=1$ band

$$\begin{aligned}\mathcal{N}_1(N,L) &= \langle N,v=1|P^L_{00}|N,v=1\rangle,\\ &= \frac{2L+1}{2(N-1)!}\int_0^\pi d\beta\sin\beta P_L(\cos\beta)\\ &\quad\times\langle 0|(bb'+\xi_1p_1p_{-1})b^{N-2}(b^\dagger_Rb'^\dagger_R+\xi_1p^\dagger_{1\,R}p^\dagger_{-1\,R})(b^\dagger_R)^{N-2}|0\rangle. \qquad (2.43)\end{aligned}$$

To evaluate the intrinsic matrix element, one needs the following derivatives

$$\begin{aligned}\Big(\frac{\partial b^\dagger_R}{\partial p^\dagger_{\pm1}}\Big) &= x_1d^1_{\pm10},\\ \Big(\frac{\partial b'^\dagger_R}{\partial p^\dagger_{\pm1}}\Big) &= x_1'd^1_{\pm10},\\ \Big(\frac{\partial p^\dagger_{\pm1\,R}}{\partial b^\dagger}\Big) &= x_1d^1_{0\pm1},\\ \Big(\frac{\partial p^\dagger_{\pm1\,R}}{\partial b'^\dagger}\Big) &= x_1'd^1_{0\pm1},\\ \Big(\frac{\partial p^\dagger_{\pm1\,R}}{\partial p^\dagger_{\pm1}}\Big) &= d^1_{\pm1\pm1},\\ \Big(\frac{\partial p^\dagger_{\pm1\,R}}{\partial p^\dagger_{\mp1}}\Big) &= d^1_{\mp1\pm1}.\end{aligned}$$

Using these derivatives, the three overlaps in the intrinsic matrix element can be evaluated as

$$\begin{aligned}
&\langle 0|b^{N-1}b'(b_R^\dagger)^{N-1}b_R'^\dagger|0\rangle \\
&\quad = (N-1)!\left[Z'(\beta)[Z(\beta)]^{N-1}+(N-1)[Y(\beta)]^2[Z(\beta)]^{N-2}\right], \qquad (2.44)\\
&\langle 0|b^{N-2}p_1p_{-1}(b_R^\dagger)^{N-1}b_R'^\dagger|0\rangle \\
&\quad = (N-1)!\left[2x_1x_1'd^1_{-10}d^1_{10}[Z(\beta)]^{N-2}+(N-2)x_1^2d^1_{-10}d^1_{10}Y(\beta)[Z(\beta)]^{N-3}\right] \qquad (2.45)\\
&\langle 0|b^{N-2}p_1p_{-1}(b_R^\dagger)^{N-2}p^\dagger_{1\,R}p^\dagger_{-1\,R}|0\rangle \\
&\quad = (N-2)!\Big[(d^1_{-11}d^1_{1-1}+d^1_{-1-1}d^1_{11})[Z(\beta)]^{N-2} \\
&\qquad +(N-2)x_1^2(d^1_{-10}d^1_{0-1}d^1_{11}+d^1_{-10}d^1_{01}d^1_{1-1}+d^1_{10}d^1_{0-1}d^1_{-11}+d^1_{10}d^1_{01}d^1_{-1-1}) \\
&\qquad\quad \times[Z(\beta)]^{N-3} \\
&\qquad +\frac{(N-2)(N-3)}{2}x_1^4d^1_{10}d^1_{-10}d^1_{01}d^1_{0-1}[Z(\beta)]^{N-4}\Big]. \qquad (2.46)
\end{aligned}$$

Substituting these in the original expression and using the norm integral from (2.21), gives

$$\begin{aligned}
\mathcal{N}_1(N,L) &= (N-1)!\sum_I\sum_{l=0}^4\Big\{\frac{1}{2}(a\delta_{l0}+(2-a)\delta_{l1})F(N-1,I) \\
&\quad +\frac{1}{6}(N-1)(2-a)a(2\delta_{l0}-3\delta_{l1}+\delta_{l2})F(N-2,I) \\
&\quad +\frac{1}{3}\xi_1(2-a)r\Big[(\delta_{l0}-\delta_{l2})F(N-2,I) \\
&\qquad \frac{1}{20}(N-2)a(-5\delta_{l0}+3\delta_{l1}+5\delta_{l2}-3\delta_{l3})F(N-3,I)\Big] \\
&\quad +\xi_1^2\frac{1}{N-1}\Big[\frac{1}{3}(2\delta_{l0}+\delta_{l2})F(N-2,I) \\
&\qquad +\frac{1}{5}(N-2)a(-\delta_{l1}+\delta_{l3})F(N-3,I) \\
&\qquad +\frac{1}{210}(N-2)(N-3)a^2(7\delta_{l0}-10\delta_{l2}+3\delta_{l4})F(N-4,I)\Big]\Big\} \\
&\quad \langle L0l0|I0\rangle^2. \qquad (2.47)
\end{aligned}$$

The resulting normalizations have exactly the same form of expansion as Eq. (2.27) but the coefficients α_{nm} have different values. The exception is the first layer coefficients which remain the same, i.e., $\alpha_{nn}=1$. For the $v=1$ band, the second and third layer coefficients are given by

$$\begin{aligned}
\text{2nd layer} \;:\; &\alpha_{10}=2a-4, \quad \alpha_{21}=8a-14, \quad \alpha_{32}=21a-32, \\
&\alpha_{43}=44a-60, \quad \alpha_{54}=20(4a-5), \quad \alpha_{65}=132a-154,
\end{aligned}$$

$$\begin{aligned}
\text{3rd layer} \;:\; & \alpha_{20} = 6(a^2 - 4a + 4), \quad \alpha_{31} = 18(5a^2 - 17a + 14), \\
& \alpha_{42} = 4(114a^2 - 352a + 263), \quad \alpha_{53} = 4(470a^2 - 1330a + 907), \\
& \alpha_{64} = 4(1200a^2 - 3090a + 1957). \qquad (2.48)
\end{aligned}$$

For the $v = 2$ band, the second and third layer coefficients to power $1/N^4$ are

$$\begin{aligned}
\text{2nd layer} \;:\; & \alpha_{10} = 3a - 8, \quad \alpha_{21} = 2(5a - 13), \\
& \alpha_{32} = 8(3a - 7), \quad \alpha_{43} = 4(12a - 25), \\
\text{3rd layer} \;:\; & \alpha_{20} = 2(5a^2 - 32a + 48), \quad \alpha_{31} = 6(23a^2 - 108a + 130), \\
& \alpha_{42} = 4(153a^2 - 672a + 739). \qquad (2.49)
\end{aligned}$$

2.3 Energies

Molecular energy levels are very accurately measured, and to match that accuracy in calculations, one needs to develop the $1/N$ expansion to fairly high orders. While this is not a serious problem owing to the recent developments in computer algebra, one would still like to avoid unwieldy expressions which have little information content. This section first shows how the layer structure in the $1/N$ expansion fulfills this role by tailoring the expressions to the required accuracy with maximum efficiency in algebraic manipulations. The following subsections derive energy formulas for the ground band and discuss the ensuing variational problem. Energy formulas for the first two vibrational bands are presented at the end.

2.3.1 General Form

The general form of the $1/N$ expansion for energy levels has been conjectured in previous work [5] but not proven explicitly. Here the layer structure inherent in the $1/N$ expansion is demonstrated with an explicit calculation of one-body energies. The expectation value of a general one-body operator $\hat{n}_l = \sum_m b^\dagger_{lm} b_{lm}$, with angular momentum projection, is given by

$$\langle \hat{n}_l \rangle_L = \langle N, r | \hat{n}_l P^L_{00} | N, r \rangle / \mathcal{N}(N, L), \qquad (2.50)$$

where $\mathcal{N}(N, L)$ is the normalization. Following steps similar to Section 2.3 and introducing $F(N, L)$ from Eq. (2.27), this can be written as

$$\langle \hat{n}_l \rangle_L = \frac{1}{2N! F(N, L)} \int d\beta \sin\beta d^L_{00}(\beta) \langle 0 | b^N \hat{n}_l (b^\dagger_R)^N | 0 \rangle, \qquad (2.51)$$

The matrix element in (2.51) can be evaluated using boson calculus (derivatives of $\hat{n}_l$, as well as all all other operators that are used in this thesis, are collected in Appendix E)

$$\begin{aligned}\langle 0|b^N \hat{n}_l (b_R^\dagger)^N|0\rangle &= N!N\left(\frac{\partial b_R^\dagger}{\partial b^\dagger}\right)^{N-1}\langle 0|\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b_R}\hat{n}_l|0\rangle, \\ &= N!N[Z(\beta)]^{N-1}x_l^2 d_{00}^l, \end{aligned} \tag{2.52}$$

where $Z(\beta)$ is defined in Eq. (2.20) and x_l denotes the normalized mean fields introduced in Eq. (2.14). Because it offers a more compact notation, it is preferable to use x_1 over r in intermediate steps. In final results both will be substituted by a, i.e. $a = 2x_1^2$. Substituting (2.52) in (2.51) and coupling the d-functions via Eq. (D.1) to a single d_{00}^J, gives an integral which is of the same form as in Eq. (2.21) but with $N-1$ bosons. Thus $\langle \hat{n}_l \rangle_L$ can be written in the form

$$\langle \hat{n}_l \rangle_L = \frac{N x_l^2}{F(N,L)} \sum_J \langle L0l0|J0\rangle^2 F(N-1,J). \tag{2.53}$$

(Note that the inverse normalization factor $1/F(N,L)$ will often be dropped when intermediate steps in the calculations are given.)

Eq. (2.53) provides a typical example for the conjecture made in Section 2.3, namely, all the matrix elements can be reduced to algebraic expressions containing the normalization function. Since the algebraic manipulations required in Eq. (2.53) can be easily performed using computer algebra to any desired order in $1/N$, the knowledge of $F(N,L)$ is seen to be the only factor that could limit its accuracy.

Again, the angular momentum sums (Appendix D) and the division in Eq. (2.53) can be carried out most efficiently using Mathematica. In order to demonstrate the layer structure and expose its connection with the layers in the normalization, Eq. (2.27) is use in the evaluation of Eq. (2.53) (without substituting the coefficients α_{nm} except $\alpha_{nn} = 1$). The final result, complete to the order $1/N^4$, reads

$$\begin{aligned}\langle \hat{n}_l \rangle_L = N x_l^2 \Big\{ & 1 + \frac{1}{aN}\big(a - \bar{l}\big) + \frac{1}{2(aN)^2}\Big(2a^2 - 4a\bar{l} + \bar{l}^2 - (2a + 2\bar{l})\alpha_{10} + \bar{l}\alpha_{21}\Big) \\ & + \frac{1}{3!(aN)^3}\Big(6a^3 - 18\bar{l}a^2 + 9\bar{l}^2 a - \bar{l}^3 + 3(-4a^2 - 4\bar{l}a + \bar{l}^2 - 2(a+\bar{l})\alpha_{10})\alpha_{10} \\ & \qquad + 3\bar{l}(3a + \alpha_{10})\alpha_{21} - \bar{l}^2\alpha_{32} + 3(2a + \bar{l})\alpha_{20} - \bar{l}\alpha_{31}\Big) \\ & + \frac{1}{4!(aN)^4}\Big(24a^4 - 96\bar{l}a^3 + 72\bar{l}^2 a^2 - 16\bar{l}^3 a + \bar{l}^4 - 24(a+\bar{l})\alpha_{10}^3 \\ & \qquad - 12(4a^2 + 4\bar{l}a - \bar{l}^2)\alpha_{10}^2 - 4(18a^3 + 18\bar{l}a^2 - 9\bar{l}^2 a + \bar{l}^3)\alpha_{10} \\ & \qquad + 12(6\bar{l}a^2 + 3\bar{l}a\alpha_{10} + \bar{l}\alpha_{10}^2)\alpha_{21} - 4(4\bar{l}^2 a + \bar{l}^2\alpha_{10})\alpha_{32} + \bar{l}^3\alpha_{43}\end{aligned}$$

$$
\begin{aligned}
&+6(10a^2+4\bar{l}a-\bar{l}^2+(6a+4\bar{l})\alpha_{10}-\bar{l}\alpha_{21})\alpha_{20}\\
&-4(4\bar{l}a+\bar{l}\alpha_{10})\alpha_{31}+\bar{l}^2\alpha_{42}-4(3a+\bar{l})\alpha_{30}+\bar{l}\alpha_{41}\Big)\\
&+\frac{\bar{L}}{(aN)^2}\Big[-a+\bar{l}+\frac{1}{3aN}\Big(-6a^2+12a\bar{l}-3\bar{l}^2+2\bar{l}-6a\alpha_{10}+3(a+\bar{l})\alpha_{21}-2\bar{l}\alpha_{32}\Big)\\
&+\frac{1}{4!(aN)^2}\Big(-72a^3+216\bar{l}a^2+4\bar{l}(-27\bar{l}+16)a+12\bar{l}^3-20\bar{l}^2+16\bar{l}\\
&-24(3a+\bar{l})\alpha_{10}^2+4(-24a^2+12a\bar{l}-3\bar{l}^2+4\bar{l})\alpha_{10}\\
&+6(10a^2+10\bar{l}a-\bar{l}^2+(6a+8\bar{l})\alpha_{10}-\bar{l}\alpha_{21})\alpha_{21}\\
&-4\bar{l}(16a+\bar{l}+4\alpha_{10})\alpha_{32}+\bar{l}(9\bar{l}-4)\alpha_{43}\\
&+36a\alpha_{20}-4(3a+2\bar{l})\alpha_{31}+4\bar{l}\alpha_{42}\Big)\Big]\\
&+\frac{\bar{L}^2}{4!(aN)^4}\Big[12a^2-24a\bar{l}+6\bar{l}^2-4\bar{l}+12(-3a+\bar{l})\alpha_{10}+6(6a+\bar{l})\alpha_{21}\\
&-4(3a+5\bar{l})\alpha_{32}+9\bar{l}\alpha_{43}\Big]\Big\}. \qquad (2.54)
\end{aligned}
$$

Although Eq. (2.54) is derived for the one-body terms in the Hamiltonian, the same structure (i.e., the N and $\bar{L}$ dependence, and the distribution of layers in α_{nm}) persists also in the case of higher order interactions. In order to facilitate the discussion of various terms in the expansion, a generic form for the expectation value of a ν-body scalar operator $\hat{O}$ is introduced

$$\langle\hat{O}\rangle_L = N^\nu \sum_{nm}\left(\frac{\bar{L}}{(aN)^2}\right)^n \frac{O_{nm}}{(aN)^m}, \qquad (2.55)$$

where the expansion coefficients O_{nm} are functions of α_{nm} and the mean field a as in Eq. (2.54). Note that due to cancellations between the numerator and the denominator, the $\bar{L}/N$ dependence in the normalization function has become $\bar{L}/N^2$ in (2.55). This is essential for the convergence of the series, as otherwise matrix elements for $L = N$ would become a power series in N and diverge. The $k+1$ terms in the expansion which have $n+m=k$ constant are referred to as the k'th layer. The N and $\bar{L}$ dependence of the k'th layer is the same as the k'th power of the first layer. Thus one can consider the double expansion $1/N$ and $\bar{L}$ as a single expansion in layers. Below the significance of each layer is discussed in turn.

0th layer (O_{00}): The leading term in (2.54) is the same as the mean field result in (2.4), which establishes the validity of the mean field theory at the limit of large N ($N \to \infty$). Naturally, O_{00} is independent of projection.

1st layer (O_{01}, O_{10}): The first one gives the $1/N$ correction to the ground energy and the second, the leading contribution to the moment of inertia. If the rotational band in question is measured only to low-spins ($L < 10$), the knowledge of the

first layer terms is quite sufficient for its description. Note that there is no α_{nm} dependence in the first layer but that is because $\alpha_{nn} = 1$ has been used. Otherwise there would be α_{nn} dependence in the first layer.

2nd layer (O_{02}, O_{11}, O_{20}): These terms represent, respectively, the $1/N^2$ correction to the ground energy, $1/N$ correction to the moment of inertia, and the leading order contribution to the deviation from rigid rotor behaviour. If a rotational band is known to spins $10 < L < 20$, this last term, which is a measure of the softness of a rotor, is essential in its description. Terms in the second layer seen to depend on α_{nn-1}, that is, the second layer coefficients in the normalization (see Appendix A), but no higher.

3rd layer $(O_{03}, O_{12}, O_{21}, O_{30})$: The first three represent the higher order corrections to the second layer terms. The last one is a correction to the softness parameter which is important in description of high-spin states ($L > 20$). Eq. (2.54) contains only the O_{02}, O_{11} terms from the third layer, which are seen to depend on α_{nn-1} and α_{nn-2}, i.e., up to the third layer coefficient in the normalization.

In addition, Eq. (2.54) contains the O_{04} term from the fourth layer, which depends on α_{nm} up to the fourth layer. The connection between the layers in the normalization and the matrix elements should be clear from the above discussion: In order to calculate the matrix elements up to the k'th layer, one needs to know the coefficients α_{nm} up to that layer (to order $1/N^{2k}$). This is very useful in higher order calculations as it restricts the number of terms needed in the normalization, excluding those which are most complex. Another computational advantage in using layers is that the length of terms O_{nm} increases exponentially with m, and terminating the series in m earlier reduces the amount of algebra enormously. For example, in Eq. (2.54), terms to the second layer take only a few lines, and the bulk of the expression is occupied by the O_{03}, O_{12} terms from the third layer and O_{04} from the fourth layer. When one fits a rotational band with the form $C_0 + C_1\bar{L} + C_2\bar{L}^2$, the coefficient C_0 is determined most accurately and the others are increasingly less so. In a second layer calculation, C_0, C_1 and C_2 are evaluated to order $1/N^2$, $1/N$, and 1, respectively, which meets this hierarchical requirement in accuracy perfectly. From a practical point of view, the accuracy offered by the higher order terms is never required. Thus on both physical and computational grounds, use of layers is a more sensible approach than a complete calculation to a given order in $1/N$. Further utility of the layer approach will be seen later when the variational problem is discussed.

2.3.2 Ground Band

Rotational bands in diatomic molecules are measured up to quite high spins ($L > 20$), which necessitates calculation of the expectation value of the Hamiltonian to the third layer. As the complexity of calculations increases substantially with the order of the interaction, the one- two- and three-body terms in Eqs. (1.12) and (2.1) are considered separately, in that order. The expectation value of $\hat{L} \cdot \hat{L}$ gives $\bar{L} = L(L+1)$ as expected from rotational invariance. Since it doesn't play any role in the dynamics of the system, it is not considered further in this section.

The expectation value for a general one-body operator has already been discussed in detail in the last subsection. Here the result for $\hat{n}_p$ is presented, extended to the third layer

$$\begin{aligned}\langle \hat{n}_p \rangle_L = \frac{aN}{2}\Big\{1 - \frac{2-a}{aN} \\ + \frac{\bar{L}}{(aN)^2}(2-a)\Big[1 + 2(1-a)\Big(\frac{1}{aN} + \frac{3-2a}{(aN)^2}\Big)\Big] \\ - \frac{\bar{L}^2}{(aN)^4}(2-a)(1-a)\Big[1 + \frac{8-7a}{aN}\Big] \\ + \frac{\bar{L}^3}{(aN)^6}2(2-a)(1-a)^2\Big\}. \end{aligned} \tag{2.56}$$

For $a = 1$, Eq. (2.56) reduces to

$$\langle \hat{n}_p \rangle_L = \frac{N}{2}\Big(1 - \frac{1}{N} + \frac{\bar{L}}{2N^2}\Big), \tag{2.57}$$

in agreement with the O(4) result given in Eq. (A.8). Note that after the substitution of α_{nm} in Eq. (2.54), all the complicated O_{0m} terms with $m > 1$ have vanished in (2.56), leading to a finite expansion for $L = 0$. This is a general feature of the ground energy that will emerge from the expectation values of all the other terms in the Hamiltonian.

There are two two-body interaction terms in Eq. (1.12). The operator $\hat{n}_p^2$ is considered first as an example, to demonstrate the basic technique involved in the evaluation of two-body terms. To simplify the calculations, it is rewritten in the normal ordered form

$$\hat{n}_p^2 = :\hat{n}_p^2: + \hat{n}_p, \quad :\hat{n}_p^2: = \sum_{\mu\mu'} p_\mu^\dagger p_{\mu'}^\dagger p_\mu p_{\mu'}, \tag{2.58}$$

where colons denote normal ordered operator. Here the second term is an effective one-body operator that results from the contraction of boson operators. Since its expectation value has already been evaluated in (2.56), it is only necessary to do

the calculation for the first term. The projected expectation value for $\hat{n}_p^2$ is given by

$$\langle \hat{n}_p^2 \rangle_L = \frac{1}{2N!F(N,L)} \int d\beta \sin\beta d_{00}^L(\beta) \langle 0|b^N(:\hat{n}_p^2:+\hat{n}_p)(b_R^\dagger)^N|0\rangle, \tag{2.59}$$

Using boson calculus, the matrix element for the first term in (2.59) can be evaluated as

$$\langle 0|b^N:\hat{n}_p^2:(b_R^\dagger)^N|0\rangle = N!N(N-1)[Z(\beta)]^{N-2}\left(x_1^2 d_{00}^1\right)^2. \tag{2.60}$$

After substituting (2.60) in (2.59) and coupling all the d-functions to a single d_{00}^J, the standard form for the β integral in Eq. (2.21) is again recovered but with $N-2$ bosons. Thus $\langle \hat{n}_p^2 \rangle_L$ becomes

$$\langle \hat{n}_p^2 \rangle_L = \frac{a^2 N(N-1)}{4F(N,L)} \sum_{lJ} \langle 1010|l0\rangle^2 \langle L0l0|J0\rangle^2 F(N-2,J) + \langle \hat{n}_p \rangle_L. \tag{2.61}$$

The rest of the algebraic manipulations in (2.61) can be carried out using Mathematica, leading to the third layer result

$$\begin{aligned}\langle \hat{n}_p^2 \rangle_L = \frac{(aN)^2}{4}\Big\{1 &- \frac{2-a}{aN} + \frac{2(2-a)}{(aN)^2} \\ &+ \frac{\bar{L}}{(aN)^2} 2(2-a)\left[1 - \frac{1+a}{aN} - \frac{2+a-2a^2}{(aN)^2}\right] \\ &+ \frac{\bar{L}^2}{(aN)^4}(2-a)\left[a + \frac{2+6a-7a^2}{aN}\right] \\ &- \frac{\bar{L}^3}{(aN)^6} 2a(2-a)(1-a)\Big\}.\end{aligned} \tag{2.62}$$

The second two-body term in (1.12) is the dipole interaction, which has the normal ordered form

$$\hat{D}\cdot\hat{D} = :\hat{D}\cdot\hat{D}: + 3\hat{n}_s + \hat{n}_p, \tag{2.63}$$

The expectation value of $\hat{n}_s$ can be obtained from that of $\hat{n}_p$ using the conservation of boson number which stipulates

$$\langle \hat{n}_s \rangle_L + \langle \hat{n}_p \rangle_L = N. \tag{2.64}$$

Following the steps outlined above, the expectation value of $\hat{D}\cdot\hat{D}$ can be reduced to the form

$$\langle \hat{D}\cdot\hat{D} \rangle_L = \frac{a(2-a)N(N-1)}{2F(N,L)} \sum_{l=0}^{1} \sum_J \langle L0l0|J0\rangle^2 F(N-2,J) + 3\langle \hat{n}_s \rangle_L + \langle \hat{n}_p \rangle_L. \tag{2.65}$$

Mathematica evaluation of Eq. (2.65) to the third layer gives

$$\langle \hat{D}\cdot\hat{D}\rangle_L = aN^2\Big\{2-a+\frac{1+2a-a^2}{aN} - \frac{\bar{L}}{(aN)^2}(2-a)\Big[2a-1-2(1-a)^2\Big(\frac{1}{aN}+\frac{3-2a}{(aN)^2}\Big)\Big] - \frac{\bar{L}^2}{(aN)^4}(2-a)(1-a)^2\Big[1+\frac{8-7a}{aN}\Big] + \frac{\bar{L}^3}{(aN)^6}2(2-a)(1-a)^3\Big\}. \tag{2.66}$$

For $a=1$, Eq. (2.66) reduces to

$$\langle \hat{D}\cdot\hat{D}\rangle_L = N^2+2N-\bar{L}, \tag{2.67}$$

in agreement with Eq. (A.3), obtained from the O(4) Casimir operator.

The three-body interactions in Eq. (2.1) are now considered. Of the three terms in (2.1), $\hat{n}_p\hat{L}^2$ is the easiest to evaluate because the states have good angular momentum. Its expectation value is trivially given by

$$\langle \hat{n}_p\hat{L}^2\rangle_L = \langle \hat{n}_p\rangle_L\bar{L}. \tag{2.68}$$

Calculation of the expectation value of $\hat{n}_p^3$ follows similar lines to the previous, lower order ones. To establish the pattern, a few key steps are shown here. The normal ordered form for $\hat{n}_p^3$ is given by

$$\hat{n}_p^3 = :\hat{n}_p^3: +3\hat{n}_p^2-2\hat{n}_p. \tag{2.69}$$

The intrinsic matrix element for the normal ordered part is

$$\langle 0|b^N:\hat{n}_p^3:(b_R^\dagger)^N|0\rangle = N!N(N-1)(N-2)[Z(\beta)]^{N-3}\left(x_1^2d_{00}^1\right)^3. \tag{2.70}$$

After combining the d-functions and substituting the β integral, the expectation value can be reduced to the form

$$\langle \hat{n}_p^3\rangle_L = \frac{a^3N(N-1)(N-2)}{8F(N,L)}\sum_{ll'J}\langle 1010|l0\rangle^2\langle 10l0|l'0\rangle^2\langle L0l'0|J0\rangle^2 \times F(N-3,J)+3\langle \hat{n}_p^2\rangle_L-2\langle \hat{n}_p\rangle_L. \tag{2.71}$$

Finally, Mathematica evaluation of Eq. (2.71) gives the following third layer result

$$\langle \hat{n}_p^3\rangle_L = \frac{(aN)^3}{8}\Big\{1+\frac{(2-a)(2+a)}{(aN)^2} + \frac{\bar{L}}{(aN)^2}3(2-a)\Big[1-\frac{2+a}{aN}+\frac{10/3-2a+2a^2}{(aN)^2}\Big] + \frac{\bar{L}^2}{(aN)^4}3(2-a)\Big[1-\frac{2a}{N}\Big] + \frac{\bar{L}^3}{(aN)^6}(2-a)(-2+2a+a^2)\Big\}. \tag{2.72}$$

Comparing Eqs. (2.53), (2.61) and (2.71), it should be fairly clear how to generalize these results to even higher order interactions in $\hat{n}_p$. The last expectation value to be considered is the second term in (2.1). This operator has a more complicated normal ordered form

$$\hat{n}_p\hat{D}\cdot\hat{D}+\hat{D}\cdot\hat{D}\hat{n}_p =: \hat{n}_p\hat{D}\cdot\hat{D}+\hat{D}\cdot\hat{D}\hat{n}_p : +2\hat{n}_p^2+2\hat{n}_p, \tag{2.73}$$

where,

$$\begin{aligned} &: \hat{n}_p\hat{D}\cdot\hat{D}+\hat{D}\cdot\hat{D}\hat{n}_p : \\ &= 2\sum_{mn}\Big[p_m^\dagger s^\dagger s^\dagger p_m p_n p_{-n} + 2p_m^\dagger p_n^\dagger s^\dagger p_m p_n s + p_m^\dagger p_n^\dagger p_{-n}^\dagger p_m ss \\ &\qquad +5p_m^\dagger s^\dagger p_m s + s^\dagger s^\dagger p_m p_{-m} + p_m^\dagger p_{-m}^\dagger ss\Big] \end{aligned} \tag{2.74}$$

contains both two- and three-body parts. The relevant derivatives are

$$\frac{\partial^3}{(\partial b^\dagger)^3}\frac{\partial^3}{\partial b_R^3} : \hat{n}_p\hat{D}\cdot\hat{D}+\hat{D}\cdot\hat{D}\hat{n}_p : \;= 72\,x_1^4x_0^2d_{00}^1(1+d_{00}^1), \tag{2.75}$$

$$\frac{\partial^2}{(\partial b^\dagger)^2}\frac{\partial^2}{\partial b_R^2} : \hat{n}_p\hat{D}\cdot\hat{D}+\hat{D}\cdot\hat{D}\hat{n}_p : \;= 8\,x_1^2x_0^2(2+5d_{00}^1). \tag{2.76}$$

The expectation value can then be obtained in the reduced form

$$\begin{aligned} &\langle : \hat{n}_p\hat{D}\cdot\hat{D}+\hat{D}\cdot\hat{D}\hat{n}_p :\rangle_L \;= \\ &\qquad \frac{N(N-1)a(2-a)}{2F(N,L)}\sum_{lJ}\langle l0L0|J0\rangle^2\Big[(2\delta_{l0}+5\delta_{l1})F(N-2,J) \\ &\qquad +\frac{a}{3}(N-2)(\delta_{l0}+3\delta_{l1}+2\delta_{l2})F(N-3,J)\Big]. \end{aligned} \tag{2.77}$$

The full $1/N$ expansion result is

$$\begin{aligned} \langle\hat{n}_p\hat{D}^2+\hat{D}^2\hat{n}_p\rangle_L = a^2N^3\Big\{&2-a+\frac{1}{aN}-\frac{(2-a)(1+a^2)}{(aN)^2} \\ &+\frac{\bar{L}}{(aN)^2}3(2-a)\Big[1-a+\frac{1-a+a^2}{aN}+\frac{2(1-a)(4/3-2a+a^2}{(aN)^2}\Big] \\ &-\frac{\bar{L}^2}{(aN)^4}(2-a)\Big[1+\frac{3(1-a)(3-4a+2a^2)}{aN}\Big] \\ &+\frac{\bar{L}^3}{(aN)^6}(2-a)(1-a)(2-2a+a^2)\Big\}. \end{aligned} \tag{2.78}$$

The general form of the $1/N$ expressions was discussed in the last subsection. Here the projected energies for the one-and two-body terms are compared with those obtained in the mean field theory, Eq. (2.4), and make a few observations on

common features of the expectation values. Rewriting the energy surface (2.4) in terms of a yields

$$E(a) = \varepsilon\frac{aN}{2} + \sigma\frac{(aN)^2}{4}\left(1 + \frac{2-a}{aN}\right) - \kappa aN^2\left(2 - a + \frac{3 - 3a + a^2}{aN}\right) + \kappa' aN. \quad (2.79)$$

Comparing Eqs. (2.56), (2.62) and (2.66) with the corresponding terms in (2.79), it is seen that the leading terms agree but the next order $(1/N)$ terms differ. The $\hat{L}\cdot\hat{L}$ interaction forms an exceptional case in that its leading term vanishes and the remaining part in (2.79) is entirely spurious. The above example explicitly shows that the mean field theory is valid in the large N limit. Thus, one should consider only the leading order terms in the energy surface and ignore the $1/N$ corrections that are not complete. An easy way to achieve this is to use the Hamiltonian in normal ordered form in mean field calculations. In this manner, one automatically excludes the $1/N$ terms arising from the contraction of boson operators, and thereby avoids potential pitfalls that could arise from odd-multipole interactions such as $\hat{L}\cdot\hat{L}$.

As remarked earlier, the ground energy ($L = 0$) has a finite expansion in $1/N$, regardless of the type of interaction used. A finite expansion is usually the hallmark of an exactly solvable model as in the case of dynamical symmetries. Another remark concerns the common factors of $(2 - a)$ in the moment of inertia (MOI) terms. In the limit of $a \to 2$, $r \to \infty$, which corresponds to a dissociated molecule with an infinite MOI. Hence the factors of $(2-a)$ simply ensure that no rotational excitation of such a molecule is possible. These factors arise directly from projection, and thus provide a non-trivial check on the accuracy of calculations.

2.3.3 Variation after Projection

Since there is only one variational parameter in the boson system, which is to be determined from the ground band, the variational problem is considered before moving on to the vibrational bands. The simplicity of the vibron model allows an analytical solution for variation after projection, without resorting to iterative numerical techniques as is usually the case in Hartree-Bose problems (e.g. the IBM). This, in turn, permits writing of the energy expressions directly in terms of the Hamiltonian parameters, an endowment which is normally reserved for dynamical symmetries. In order to take full advantage of the $1/N$ expansion in the solution process, we first scale the strength of the interactions, so that their expectation values have the same N dependence to leading order. Further, since the dipole interaction dominates the Hamiltonian, its strength sets the energy scale of the spectrum. Thus, we factor out κN^2 from the energy expressions, and introduce the

dimensionless strength parameters for the other interactions as

$$\eta_1 = \frac{\varepsilon}{4N\kappa}, \quad \eta_2 = \frac{\sigma}{4\kappa}, \quad \eta_3 = \frac{3N\tau_1}{16\kappa}, \quad \eta_3' = \frac{N\tau_2}{2\kappa}, \quad \eta_3'' = \frac{N\tau_3}{2\kappa}. \tag{2.80}$$

The numerical factors in (2.80) are chosen for convenience to simplify the expressions. For small perturbations of the O(4) limit, the strength parameters η_i should all be much less then 1.

Adding all the contributions from Eqs. (2.56), (2.62), (2.66), (2.72) and (2.78), one obtains a rather lengthy expression for the ground-band energies. In discussing the variational problem, it will be more convenient to express it in a compact form. Thus, following the general form in Eq. (2.55), we rewrite the ground-band energy as

$$E_{g,L}(a) = \kappa N^2 \sum_{nm} \frac{C_{nm}}{N^m} \left(\frac{\bar{L}}{N^2}\right)^n. \tag{2.81}$$

The coefficients C_{nm} in Eq. (2.81) can be read off from the respective contributions in the last subsection. For example, the coefficients for the zeroth and first layer are given by

$$\begin{aligned} C_{00} &= -a(2-a) + 2\eta_1 a + \eta_2 a^2 + 2\eta_3 a^3/3 + 2\eta_3' a^2(2-a), \\ C_{01} &= -(1+2a-a^2) - 2\eta_1(2-a) - \eta_2 a(2-a) + 2\eta_3' a, \\ C_{10} &= (2-a)[(2a-1)/a + 2\eta_1/a + 2\eta_2 + 2\eta_3 a + 6\eta_3'] + \eta_3'' a, \end{aligned} \tag{2.82}$$

where the scaled parameters from (2.80) have been substituted. The minimum of the ground energy is obtained from

$$\frac{dE_{g,L}(a)}{da} = 0, \tag{2.83}$$

which can be solved algebraically using an ansatz similar to (2.81)

$$a = \sum_{nm} \frac{a_{nm}}{N^m} \left(\frac{\bar{L}}{N^2}\right)^n. \tag{2.84}$$

Use of the layers approach again simplifies solution of the variational equation. Substituting the ansatz (2.84) in (2.83), it can be shown that each layer leads to an independent set of equations. Thus starting from the zeroth layer, one can construct the solution layer by layer. For the leading order (zeroth layer), one has the Hartree-Bose equation

$$\left.\frac{dC_{00}}{da}\right|_{a_{00}} = 0. \tag{2.85}$$

In the following, a_{00} s denoted by a_0 for notational convenience. Using the expression for C_{00}, Eq. (2.82) in (2.85), gives the following quadratic equation for a_0

$$-1 + \eta_1 + (1 + \eta_2 + 4\eta_3')a_0 + (\eta_3 - 3\eta_3')a_0^2 = 0. \tag{2.86}$$

Since $a \geq 0$, take the positive root of this equation

$$a_0 = \frac{1}{2(\eta_3 - 3\eta_3')}\left[-(1+\eta_2+4\eta_3') + \left((1+\eta_2+4\eta_3')^2 + 4(1-\eta_1)(\eta_3-3\eta_3')\right)^{1/2}\right]. \tag{2.87}$$

This solution leads to an indeterminate result when the cubic terms vanish. To obtain a more transparent result, we expand it for small cubic strength

$$a_0 = \frac{1-\eta_1}{1+\eta_2+4\eta_3'}\left[1 - \frac{(1-\eta_1)(\eta_3-3\eta_3')}{(1+\eta_2+4\eta_3')^2} + 2\left(\frac{(1-\eta_1)(\eta_3-3\eta_3')}{(1+\eta_2+4\eta_3')^2}\right)^2 - \ldots\right]. \tag{2.88}$$

For the one- and two-body parts of the Hamiltonian, i.e. for $\eta_3 = \eta_3' = 0$ in (2.88), one obtains a very simple result for a_0

$$a_0 = (1-\eta_1)/(1+\eta_2). \tag{2.89}$$

When all $\eta << 1$, corresponding to small perturbations of the O(4) limit, Eq. (2.88) gives to leading order

$$a_0 = 1 - \eta_1 - \eta_2 - \eta_3 - \eta_3', \tag{2.90}$$

which explains the choice of the numerical factors in Eq. (2.80). With the exception of η_3'', all the symmetry breaking terms with equal scaled strength η lead to an equivalent change in the size parameter.

Once a_0 is determined, the next layer in the solution, a_{01} and a_{10}, are obtained by solving the respective set of equations for the first layer

$$\begin{aligned} \left.\frac{dC_{00}}{da}\right|_{a_0+a_{01}/N} &= -\frac{1}{N}\left.\frac{dC_{01}}{da}\right|_{a_0}, \\ \left.\frac{dC_{00}}{da}\right|_{a_0+a_{10}\bar{L}/N^2} &= -\frac{\bar{L}}{N^2}\left.\frac{dC_{10}}{da}\right|_{a_0}. \end{aligned} \tag{2.91}$$

Upon substituting the mean fields in the derivatives in (2.91), the leading order vanishes by virtue of the Hartree-Bose equation (2.85). The next order leads to trivial linear equations for a_{01} and a_{10} that can be solved to give

$$\begin{aligned} a_{01} &= \frac{1-\eta_1+\eta_2-\eta_3'-(1+\eta_2)a_0}{1+\eta_2+4\eta_3'+2(\eta_3-3\eta_3')a_0}, \\ a_{10} &= \frac{1-(1-2\eta_1)/a_0^2+\eta_2-2\eta_3(1-a_0)+3\eta_3'-\eta_3''}{1+\eta_2+4\eta_3'+2(\eta_3-3\eta_3')a_0}. \end{aligned} \tag{2.92}$$

Substituting a_0 from (2.87), the coefficients a_{01} and a_{10} can be determined directly in terms of the Hamiltonian parameters. These general expressions are somewhat

complicated, so they are not quoted here. When only the one- and two-body parts are considered, they reduce to particularly simple forms given by

$$a_{01} = \frac{\eta_2}{1+\eta_2}, \quad a_{10} = \frac{\eta_1^2 + 2\eta_1\eta_2 - \eta_2}{(1-\eta_1)^2}. \tag{2.93}$$

A question of general interest here is the the difference between variation after and before projection (VAP and VBP) results. In VBP, one substitutes the leading order mean field (a_0), obtained from the Hartree-Bose equation, in the energy expression (2.81). Whereas in VAP, the full solution for the mean field (2.84) is used. Thus, the difference between VAP and VBP arises from the contribution of the higher order mean fields to the ground energy. From the Taylor expansion of $E_{g,L}(a)$ and the Hartree-Bose condition (2.85), it is clear that contribution of the first layer mean fields to the first layer in the ground energy vanishes, and these correction terms due to VAP appear only at the second and higher layers. This holds in general for all layers, in that, the corrections due to a given layer in the mean fields appear in the next and higher levels in the energy. Therefore, VAP and VBP give the same results for the first layer (i.e. leading terms in band excitation energies and moment of inertia), but differ in the second and higher layers.

The above argument indicates that for the third layer expansion considered here, one needs at most the second layer mean fields a_{02}, a_{11} and a_{20}. These are obtained from the set of equations

$$\begin{aligned}
\left.\frac{dC_{00}}{da}\right|_{a_0+a_{01}/N+a_{02}/N^2} &= -\frac{1}{N}\left.\frac{dC_{01}}{da}\right|_{a_0+a_{01}/N} - \frac{1}{N}\left.\frac{dC_{02}}{da}\right|_{a_0}, \\
\left.\frac{dC_{00}}{da}\right|_{a_0+a_{10}\bar{L}/N^2+a_{20}\bar{L}^2/N^4} &= -\frac{\bar{L}}{N^2}\left.\frac{dC_{10}}{da}\right|_{a_0+a_{10}\bar{L}/N^2} - \frac{\bar{L}^2}{N^4}\left.\frac{dC_{20}}{da}\right|_{a_0}, \\
\left.\frac{dC_{00}}{da}\right|_{a_0+a_{01}/N+a_{10}\bar{L}/N^2+a_{11}\bar{L}/N^3} &= -\frac{1}{N}\left.\frac{dC_{01}}{da}\right|_{a_0+a_{10}\bar{L}/N^2} - \frac{\bar{L}}{N^2}\left.\frac{dC_{10}}{da}\right|_{a_0+a_{01}/N} \\
&\quad -\frac{\bar{L}}{N^3}\left.\frac{dC_{11}}{da}\right|_{a_0}.
\end{aligned} \tag{2.94}$$

Again, after substituting the mean fields, the zeroth and first layer parts of these equations vanish by virtue of Eqs. (2.85) and (2.91), leaving behind trivial linear equations for the second layer mean fields.

The resulting mean fields and the energy expressions are rather lengthy when the cubic terms are included. Therefore, the presentation of the complete third layer results is restricted to the one- and two-body terms in the Hamiltonian. This will make the comparisons between VAP and VBP easier. To this end, the explicit

expression for $E_{g,L}(a)$ is

$$
\begin{aligned}
E_{g,L}(a) = \kappa N^2 \Big\{ & a\,(a-2+2\eta_1+a\eta_2) \\
& + \frac{1}{N}\big(-1-2a+a^2\big) - 2(2-a)\eta_1 - a(2-a)\eta_2\big) + \frac{2}{N^2}(2-a)\eta_2 \\
& + \frac{\bar{L}}{N^2}\frac{2-a}{a}\Big[2a-1+2\eta_1+2a\eta_2 - \frac{2}{aN}\big((1-a)(1-a-2\eta_1) + a(1+a)\eta_2\big)\big) \\
& \qquad - \frac{2}{(aN)^2}\big((1-a)(3-2a)(1-a-2\eta_1) + a(2+a-2a^2)\eta_2\big)\Big] \\
& + \frac{\bar{L}^2}{N^4}\frac{2-a}{a^3}\Big[(1-a)(1-a-2\eta_1) + a^2\eta_2 \\
& \qquad + \frac{1}{aN}\big((1-a)(7-8a)(1-a-2\eta_1) + a(2+6a-7a^2)\eta_2\big)\Big] \\
& - \frac{\bar{L}^3}{N^6}\frac{2}{a^5}(2-a)(1-a)\big((1-a)(1-a-2\eta_1) + a^2\eta_2\big)\Big\}. \qquad (2.95)
\end{aligned}
$$

The solution of the variational problem for (2.95) has been given in Eqs. (2.89) and (2.93) for the zeroth and first layers, respectively. Extending this solution for a to the second layer gives

$$
\begin{aligned}
a = & \frac{1-\eta_1}{1+\eta_2} + \frac{1}{N}\frac{\eta_2}{1+\eta_2} \\
& + \frac{\bar{L}}{N^2}\frac{1}{(1-\eta_1)^2}\Big[\eta_1^2 + 2\eta_1\eta_2 - \eta_2 + \frac{1}{N}\frac{2}{1-\eta_1} \\
& \qquad \times\big(\eta_1^2(1+\eta_1+4\eta_2) - \eta_2 + \eta_2^2(3\eta_1-2)\big)\Big] \\
& + \frac{\bar{L}^2}{N^4}\frac{1+\eta_2}{(1-\eta_1)^5}(\eta_1^2 + 2\eta_1\eta_2 - \eta_2)(\eta_1^2 - \eta_1\eta_2 - 3\eta_1 - \eta_2). \qquad (2.96)
\end{aligned}
$$

When $\eta_1 = \eta_2 = 0$, Eq. (2.96) reduces to $a = 1$, consistent with the O(4) limit. Thus, there is no difference between VAP and VBP in the O(4) limit. Finally, substituting (2.96) in (2.95), gives the following expression for the ground-band energies, directly in terms of the Hamiltonian parameters

$$
\begin{aligned}
E_{g,L} = \kappa N^2 \Big\{ & -\frac{1}{1+\eta_2}\Big[(1-\eta_1)^2 + \frac{1}{N}(2+2\eta_1+\eta_1^2+2\eta_1\eta_2+3\eta_2) \\
& \qquad - \frac{1}{N^2}(2+2\eta_1+3\eta_2)\eta_2 + \frac{1}{N^3}\eta_2^2\Big] \\
& + \frac{\bar{L}}{N^2}\frac{1}{1-\eta_1}\Big[1+\eta_1+2\eta_2 \\
& \qquad + \frac{1}{N}\frac{2}{1-\eta_1}\big((1+\eta_1)\eta_1^2 - (2-\eta_1-4\eta_1^2)\eta_2 - (3-4\eta_1)\eta_2^2\big) \\
& \qquad + \frac{1}{N^2}\frac{2}{(1-\eta_1)^2}\big((1+\eta_1)(1+2\eta_1)\eta_1^2 - (1+3\eta_1-6\eta_1^2-12\eta_1^3)\eta_2
\end{aligned}
$$

$$-(3+6\eta_1-20\eta_1^2)\eta_2^2-(5-8\eta_1)\eta_2^3)\Big)\Big]$$
$$-\frac{\bar{L}^2}{N^4}\frac{1}{(1-\eta_1)^4}\Big[(1+\eta_2)^2(\eta_1^2+2\eta_1\eta_2-\eta_2)$$
$$+\frac{1}{N}\frac{1+\eta_2}{1-\eta_1}\Big((1+7\eta_1+4\eta_1^2-4\eta_1^3)\eta_1^2$$
$$-(1+7\eta_1-13\eta_1^2-31\eta_1^3+16\eta_1^4)\eta_2$$
$$-(3+17\eta_1-52\eta_1^2+16\eta_1^3)\eta_2^2-(6-10\eta_1)\eta_2^3\Big)\Big]$$
$$+\frac{\bar{L}^3}{N^6}\frac{2\eta_1(1+\eta_2)^4}{(1-\eta_1)^7}(\eta_1^2+2\eta_1\eta_2-\eta_2)\Big\}. \tag{2.97}$$

Eq. (2.97) is an exact result to the given order. A numerical analysis of the diagonalization results for the Hamiltonian (1.12) has been carried out, and found to directly verify that the N and $\bar{L}$ dependence of the ground-band energies are as given in (2.97). This agreement with the diagonalization results also confirms that Eq. (2.97) is free from computational errors.

The energy difference between VAP and VBP results is obtained by subtracting Eq. (2.95) with $a = a_0$ from (2.97). To the second layer, which is of most interest, it is given by

$$E_{g,L}-E_{g,L}(a_0)=-\kappa N^2\Big(\frac{1}{N^2}\frac{\eta_2^2}{1+\eta_2}+\frac{\bar{L}}{N^3}\frac{2\eta_2(\eta_1^2+2\eta_1\eta_2-\eta_2)}{(1-\eta_1)^2}$$
$$+\frac{\bar{L}^2}{N^4}\frac{(1+\eta_2)(\eta_1^2+2\eta_1\eta_2-\eta_2)^2}{(1-\eta_1)^4}\Big). \tag{2.98}$$

Thus, as expected, VAP leads to a lower ground energy than VBP. Note also that for $\eta_2 = 0$, the difference in the ground energy and MOI ($\bar{L}$) terms vanish. In fact, the equivalence of VAP and VBP for these terms holds also in the higher layers. Thus breaking of the O(4) limit with the $\hat{n}_p$ term constitutes a special case, as it partially preserves the complete equivalence of VAP and VBP found in the O(4) limit.

As a final remark on the ground-band energies (2.97), MOI systematics and its correlation with the size parameter a or r is discussed. (Note that for small perturbations of the O(4) limit $a \approx r$.) From Eqs. (2.88)-(2.90), it is seen that the equilibrium size gets smaller for positive values of η, and larger for negative values. Inspection of the MOI term in Eq. (2.97) shows that it also gets smaller for positive η, and larger for negative η. Thus the two quantities are correlated as in the geometrical models, larger size leads to a larger MOI. The same correlation holds also for the cubic terms $\hat{n}_p^3$ and $\hat{n}_p\hat{D}^2+\hat{D}^2\hat{n}_p$ but not for the $\hat{L}^2$ and $\hat{n}_p\hat{L}^2$ terms. In fact, the $\hat{L}^2$ term is completely divorced from the dynamics of the system

(the MOI remains constant as a or r changes), and the $\hat{n}_p\hat{L}^2$ term has the wrong dynamic dependence on r (the MOI decreases as r increases). Thus caution should be exercised in phenomenological uses of these terms. It would be better if they could be avoided altogether, but certainly, they should not play a dominant role in description of MOI.

2.3.4 Vibrational Bands

Calculations for the vibrational bands follow much the same lines as in the ground band, namely, i) matrix element of a given interaction is evaluated in the intrinsic frame using boson calculus, ii) all the resulting d-functions are combined to a single d^J_{00}, iii) the normalization function (2.27) with the appropriate N is substituted for the resulting β integrals. The rest of the calculations require standard algebraic manipulations that can be carried out most efficiently using Mathematica. The only difference is that there are many more terms to be evaluated and the amount of angular momentum algebra in each term gets longer. As a rule of thumb, the complexity of calculations grows exponentially with the vibrational number v. Nevertheless, the final expressions obtained are as compact as those for the ground band.

For $v << N$, the change in structure between two neighboring bands are very similar, irrespective of the value of v. Thus to get a picture of how the band structure changes with increasing v, it is quite sufficient to compare $v = 0$ and $v = 1$ bands. To this end, the ground-band calculations presented in Section 3.2 have been repeated for the $v = 1$ band. The derivatives of $\hat{n}_p$ required are given in Appendix E. Note that this appendix contains all the operator derivatives used in the calculations in this thesis. The expectation value of the one-body operator, after application of the boson calculus technique, can be reduced to the form

$$\begin{aligned}
\langle \hat{n}_p \rangle_{1,L} \;=\; & \sum_{J=0}^{5} \Big\{ \frac{2-a}{2}\delta_{J1} F(N-1,J) \\
& + \frac{a}{4}(N-1)\left((2-a)\delta_{J0} + (3a-1)\delta_{J1} + 2(2-a)\delta_{J2}\right) \times F(N-2,J) \\
& + \frac{(2-a)a^2}{60}(N-1)(N-2)\left(5\delta_{J0} - 12\delta_{J1} + 10\delta_{J2} - 3\delta_{J3}\right) F(N-3,J) \\
& + \frac{2[(2-a)a]^{1/2}\xi_1}{3}\Big[2(\delta_{J0} - \delta_{J2}) F(N-2,J) \\
& - \frac{a}{4}(N-2)\left(2\delta_{J0} - 3\delta_{J1} - 2\delta_{J2} + 3\delta_{J3}\right) F(N-3,J) \\
& + \frac{a^2}{280}(N-2)(N-3)\left(7\delta_{J0} - 21\delta_{J1} + 5\delta_{J2} + 21\delta_{J3} - 12\delta_{J4}\right) F(N-4,J) \Big]
\end{aligned}$$

$$+\xi_1^2\Big[\frac{2}{3}\,(2\delta_{J0}+\delta_{J2})\,F(N-2,J)-\frac{a}{10}(N-2)\,(2\delta_{J1}-7\delta_{J3})\,F(N-3,J)$$
$$+\frac{a^2}{70}(N-2)(N-3)\,(7\delta_{J0}-15\delta_{J2}+8\delta_{J4})\,F(N-4,J)$$
$$+\frac{a^3}{1260}(N-2)(N-3)(N-4)\,(9\delta_{J1}-14\delta_{J3}+5\delta_{J5})\,F(N-5,J)\Big]\Big\} \quad (2.99)$$

Substituting the norm integral and rearranging, gives the following $1/N$ expansion

$$\langle\hat{n}_p\rangle_{1,L}=\frac{aN}{2}\Big\{1-\frac{1}{N}$$
$$+\frac{\bar{L}}{(aN)^2}(2-a)\Big[1+\frac{2(3-a)}{aN}+\frac{2(5-a)(3-2a)}{(aN)^2}\Big]$$
$$-\frac{\bar{L}^2}{(aN)^4}(2-a)(1-a)\Big[1+\frac{3(8-3a)}{aN}\Big]$$
$$+\frac{\bar{L}^3}{(aN)^6}2(2-a)(1-a)^2\Big\}. \quad (2.100)$$

Substituting $a=1$ in Eq. (2.100) reproduces the O(4) result given in (A.8). For the two-body operators $\hat{n}_p^2$ and $\hat{D}\cdot\hat{D}$, the same intermediate steps and final expressions are given by

$$\langle\hat{n}_p^2\rangle_{1,L} = \sum_{J=0}^{6}\Big\{\frac{2-a}{2}\delta_{J1}F(N-1,J)$$
$$+\frac{a}{12}(N-1)\,(7(2-a)\delta_{J0}+3(3a-4)\delta_{J1}+14(2-a)\delta_{J2})\,F(N-2,J)$$
$$+\frac{a^2}{120}(N-1)(N-2)(5(7a-12)\delta_{J0}+3(46-23a)\delta_{J1}+10(7a-12)\delta_{J2}$$
$$+36(2-a)\delta_{J3})F(N-3,J)$$
$$+\frac{(2-a)a^3}{840}(N-1)(N-2)(N-3)\,(28\delta_{J0}-63\delta_{J1}+65\delta_{J2}-42\delta_{J3}+12\delta_{J4})$$
$$\times F(N-4,J)$$
$$+\frac{2[(2-a)a]^{1/2}\xi_1}{3}\Big[\frac{4}{3}\,(\delta_{J0}-\delta_{J2})\,F(N-2,J)$$
$$-\frac{a}{60}(N-2)(20\delta_{J0}-57\delta_{J1}-20\delta_{J2}+57\delta_{J3})F(N-3,J)$$
$$+\frac{a^2}{280}(N-2)(N-3)\,(21\delta_{J0}-35\delta_{J1}+15\delta_{J2}+35\delta_{J3}-36\delta_{J4})\,F(N-4,J)$$
$$-\frac{a^3}{5040}(N-2)(N-3)(N-4)(21\delta_{J0}-27\delta_{J1}+15\delta_{J2}+7\delta_{J3}-36\delta_{J4}+20\delta_{J5})$$
$$\times F(N-5,J)\Big]$$
$$+\xi_1^2\Big[\frac{4}{3}\,(2\delta_{J0}+\delta_{J2})\,F(N-2,J)$$
$$+\frac{a}{10}(N-2)\,(2\delta_{J1}+23\delta_{J3})\,F(N-3,J)$$

$$+\frac{a^2}{420}(N-2)(N-3)\left(154\delta_{J0}-325\delta_{J2}+276\delta_{J4}\right)F(N-4,J)$$
$$+\frac{a^3}{1260}(N-2)(N-3)(N-4)\left(54\delta_{J1}-119\delta_{J3}+65\delta_{J5}\right)F(N-5,J)$$
$$+\frac{a^4}{9240}(N-2)(N-3)(N-4)(N-5)\left(11\delta_{J0}-21\delta_{J4}+10\delta_{J6}\right)F(N-6,J)\Big]\Big\}, \tag{2.101}$$

$$\langle\hat{n}_p^2\rangle_{1,L}=\frac{(aN)^2}{4}\Big\{1+\frac{6-5a}{aN}+\frac{2a}{(aN)^2}$$
$$+\frac{\bar{L}}{(aN)^2}2(2-a)\Big[1+\frac{3(1-a)}{aN}+\frac{10-21a+6a^2}{(aN)^2}\Big]$$
$$+\frac{\bar{L}^2}{(aN)^4}(2-a)\Big[a-\frac{6-30a+13a^2}{aN}\Big]$$
$$-\frac{\bar{L}^3}{(aN)^6}2a(2-a)(1-a)\Big\}, \tag{2.102}$$

$$\langle\hat{D}\cdot\hat{D}\rangle_{1,L} = \sum_{J=0}^{5}\Big\{\frac{1}{2}\left(3a\delta_{J0}+(2-a)\delta_{J1}\right)F(N-1,J)$$
$$+\frac{1}{2}(N-1)(a(2-a)\delta_{J0}+2(5-11a+5a^2)\delta_{J1}+a(2-a)\delta_{J2})F(N-2,J)$$
$$+\frac{a(2-a)}{20}(N-1)(N-2)$$
$$\times\left(5(a+2)\delta_{J0}+(19a-20)\delta_{J1}+5(6-5a)\delta_{J2}+a\delta_{J3}\right)F(N-3,J)$$
$$+\frac{a^2(2-a)^2}{60}(N-1)(N-2)(N-3)\left(5\delta_{J0}-3\delta_{J1}-5\delta_{J2}+3\delta_{J3}\right)F(N-4,J)$$
$$+\frac{2[(2-a)a]^{1/2}\xi_1}{3}\Big[-2\left(2\delta_{J0}+\delta_{J2}\right)F(N-2,J)$$
$$+\frac{1}{4}(N-2)((16-17a)\delta_{J0}+3(4-a)\delta_{J1}+(23a-28)\delta_{J2}-3a\delta_{J3})F(N-3,J)$$
$$-\frac{a}{140}(N-2)(N-3)((35+14a)\delta_{J0}$$
$$+21(8a-13)\delta_{J1}-5(7-4a)\delta_{J2}+21(13-8a)\delta_{J3}+6a\delta_{J4})F(N-4,J)$$
$$-\frac{a^2}{70}(N-2)(N-3)(N-4)\left(7\delta_{J0}-10\delta_{J2}+3\delta_{J4}\right)F(N-5,J)\Big]$$
$$+\frac{1}{3}\xi_1^2\Big[2\left(2\delta_{J0}+\delta_{J2}\right)F(N-2,J)$$
$$+\frac{1}{10}(N-2)(70(2-a)\delta_{J0}-6a\delta_{J1}+35(2-a)\delta_{J2}+21\delta_{J3})F(N-3,J)$$
$$+\frac{a}{70}(N-2)(N-3)(7(40-17a)\delta_{J0}+105(a-2)\delta_{J1}-10(7+a)\delta_{J2}$$
$$+210(2-a)\delta_{J3}+24a\delta_{J4})F(N-4,J)$$

$$+\frac{a^2}{420}(N-2)(N-3)(N-4)(189(2-a)\delta_{J0}+9(15a-28)\delta_{J1}-360(2-a)\delta_{J2}$$
$$+28(9-5a)\delta_{J3}+171(2-a)\delta_{J4}+5a\delta_{J5})F(N-5,J)$$
$$+\frac{a^3(2-a)}{420}(N-2)(N-3)(N-4)(N-5)(21\delta_{J0}+9\delta_{J1}-30\delta_{J2}-14\delta_{J3}+9\delta_{J4}$$
$$+5\delta_{J5})F(N-6,J)\Big]\Big\}, \tag{2.103}$$

$$\langle\hat{D}\cdot\hat{D}\rangle_{1,L}=aN^2\Big\{2-a+\frac{3-10a+5a^2}{aN}$$
$$-\frac{\bar{L}}{(aN)^2}(2-a)\Big[2a-1-6(1-a)^2\Big(\frac{1}{aN}+\frac{5-2a}{(aN)^2}\Big)\Big]$$
$$-\frac{\bar{L}^2}{(aN)^4}(2-a)(1-a)^2\Big[1+\frac{24-13a}{aN}\Big]$$
$$+\frac{\bar{L}^3}{(aN)^6}2(2-a)(1-a)^3\Big\}. \tag{2.104}$$

Again, substituting $a=1$ in Eq. (2.104), one recovers the Casimir result given in (A.3). Similarly, the expectation values of the three-body operators are given by

$$\langle\hat{n}_p^3\rangle_{1,L} = \sum_{J=0}^{7}\Big\{\frac{2-a}{2}\delta_{J1}F(N-1,J)$$
$$+\frac{a}{4}(N-1)(5(2-a)(\delta_{J0}+2\delta_{J2})+(3a-4)\delta_{J1})F(N-2,J)$$
$$+\frac{a^2}{24}(N-1)(N-2)((17a-28)(\delta_{J0}+2\delta_{J2})+6(2-a)(8\delta_{J1}+5\delta_{J3}))F(N-3,J)$$
$$+\frac{a^3}{560}(N-1)(N-2)(N-3)(5(2-a)(21\delta_{J0}+54\delta_{J2}+16\delta_{J4})$$
$$+7(13a-24)(3\delta_{J1}+2\delta_{J3}))F(N-4,J)$$
$$+\frac{a^4(2-a)}{5040}(N-1)(N-2)(N-3)(N-4)(63\delta_{J0}-162\delta_{J1}+180\delta_{J2}$$
$$-133\delta_{J3}+72\delta_{J4}-20\delta_{J5})F(N-5,J)$$
$$+\frac{2[(2-a)a]^{1/2}\xi_1}{3}\Big[8\,(\delta_{J0}-\delta_{J2})\,F(N-2,J)$$
$$-\frac{a}{4}(N-2)\,(8\delta_{J0}-39\delta_{J1}-8\delta_{J2}+39\delta_{J3})\,F(N-3,J)$$
$$+\frac{a^2}{280}(N-2)(N-3)\,(385\delta_{J0}-399\delta_{J1}+275\delta_{J2}+399\delta_{J3}-660\delta_{J4})\,F(N-4,J)$$
$$-\frac{a^3}{1680}(N-2)(N-3)(N-4)(189\delta_{J0}-378\delta_{J1}+135\delta_{J2}+98\delta_{J3}$$
$$-324\delta_{J4}+280\delta_{J5})F(N-5,J)$$
$$+\frac{a^4}{36960}(N-2)(N-3)(N-4)(N-5)(99\delta_{J0}-297\delta_{J1}+165\delta_{J2}+77\delta_{J3}$$

$$
\begin{aligned}
&-144\delta_{J4}+220\delta_{J5}-120\delta_{J6})F(N-6,J)\Big]\\
&+\xi_1^2\Big[\frac{8}{3}(2\delta_{J0}+\delta_{J2})\,F(N-2,J)\\
&\quad+\frac{a}{10}(N-2)\,(22\delta_{J1}+73\delta_{J3})\,F(N-3,J)\\
&\quad+\frac{a^2}{28}(N-2)(N-3)\,(42\delta_{J0}-71\delta_{J2}+92\delta_{J4})\,F(N-4,J)\\
&\quad+\frac{a^3}{840}(N-2)(N-3)(N-4)\,(204\delta_{J1}-469\delta_{J3}+370\delta_{J5})\,F(N-5,J)\\
&\quad+\frac{a^4}{9240}(N-2)(N-3)(N-4)(N-5)\,(132\delta_{J0}-55\delta_{J2}-267\delta_{J4}+190\delta_{J6})\\
&\qquad\times F(N-6,J)\\
&\quad+\frac{a^5}{720720}(N-2)(N-3)(N-4)(N-5)(N-6)(429\delta_{J1}-364\delta_{J3}-275\delta_{J5}\\
&\qquad+210\delta_{J7})F(N-7,J)\Big]\Big\},
\end{aligned}
\tag{2.105}
$$

$$
\begin{aligned}
\langle\hat{n}_p^3\rangle_{1,L}=\frac{(aN)^3}{8}\Big\{&1+\frac{6(3-2a)}{aN}+\frac{(4-18a+11a^2)}{(aN)^2}-\frac{4a}{(aN)^3}\\
&+\frac{\bar{L}}{(aN)^2}3(2-a)\Big[1+\frac{6-7a}{aN}+\frac{2(41/3-19a+7a^2)}{(aN)^2}\Big]\\
&+\frac{\bar{L}^2}{(aN)^4}3(2-a)\Big[1-\frac{2(5-3a)}{N}\Big]\\
&+\frac{\bar{L}^3}{(aN)^6}(2-a)(-2+2a+a^2)\Big\},
\end{aligned}
\tag{2.106}
$$

$$
\begin{aligned}
\langle\hat{n}_p\hat{D}^2+\hat{D}^2\hat{n}_p\rangle_{1,L}\;=\;&\sum_{J=0}^{6}\Big\{(2-a)\delta_{J1}F(N-1,J)\\
&+\frac{1}{6}(N-1)(17a(2-a)\delta_{J0}-3(20-44a+23a^2)\delta_{J1}\\
&\qquad-14a(2-a)\delta_{J2})F(N-2,J)\\
&+\frac{a}{15}(N-1)(N-2)(5(11-14a+5a^2)\delta_{J0}+3(5+2a)(2-a)\delta_{J1}\\
&\qquad+5(46-70a+25a^2)\delta_{J2}+9a(2-a)\delta_{J3})F(N-3,J)\\
&+\frac{a^2(2-a)}{140}(N-1)(N-2)(N-3)(21a\delta_{J0}+7(10+a)\delta_{J1}-5(28-23a)\delta_{J2}\\
&\qquad+21(10-7a)\delta_{J3}+4a\delta_{J4})F(N-4,J)\\
&-\frac{a^3(2-a)^2}{420}(N-1)(N-2)(N-3)(N-4)(7\delta_{J0}-21\delta_{J1}+5\delta_{J2}+21\delta_{J3}\\
&\qquad-12\delta_{J4})F(N-5,J)\\
+2[(2-a)a]^{1/2}\xi_1\Big[&-\frac{4}{3}\,(\delta_{J0}+2\delta_{J2})\,F(N-2,J)
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{30}(N-2)(20(11-10a)\delta_{J0}+3(40-21a)\delta_{J1}-10(28-23a)\delta_{J2}\\
&\quad -57a\delta_{J3})F(N-3,J)\\
&+\frac{a}{140}(N-2)(N-3)(7(20-17a)\delta_{J0}+7(86-61a)\delta_{J1}+85a\delta_{J2}\\
&\quad -7(106-71a)\delta_{J3}-36a\delta_{J4})F(N-4,J)\\
&+\frac{a^2}{1260}(N-2)(N-3)(N-4)(63(a-3)\delta_{J0}+9(7-9a)\delta_{J1}+45(21-11a)\delta_{J2}\\
&\quad +7(13a-9)\delta_{J3}+108(4a-7)\delta_{J4}-10a\delta_{J5})F(N-5,J)\\
&-\frac{a^3(2-a)}{630}(N-2)(N-3)(N-4)(N-5)\,(9\delta_{J1}-14\delta_{J3}+5\delta_{J5})\,F(N-6,J)\Big]\\
&+\frac{1}{3}\xi_1^2\Big[8(2\delta_{J0}+\delta_{J2})F(N-2,J)\\
&+\frac{1}{5}(N-2)(140(2-a)\delta_{J0}+6a\delta_{J1}+70(2-a)\delta_{J2}+69a\delta_{J3})F(N-3,J)\\
&+\frac{a}{70}(N-2)(N-3)(14(120-49a)\delta_{J0}-42(2-a)\delta_{J1}-5(84+23a)\delta_{J2}\\
&\quad +1407(2-a)\delta_{J3}+276\delta_{J4})F(N-4,J)\\
&+\frac{a^2}{210}(N-2)(N-3)(N-4)(651(2-a)\delta_{J0}+36(5a-7)\delta_{J1}-1380(2-a)\delta_{J2}\\
&\quad +14(63-40a)\delta_{J3}+1044(2-a)\delta_{J4}+65a\delta_{J5})F(N-5,J)\\
&+\frac{a^3}{4620}(N-2)(N-3)(N-4)(N-5)(33(112-55a)\delta_{J0}+1485(2-a)\delta_{J1}\\
&-3630(2-a)\delta_{J2}-3080(2-a)\delta_{J3}+9(396-205a)\delta_{J4}+1595(2-a)\delta_{J5})\\
&\quad +30a\delta_{J6})F(N-6,J)\\
&-\frac{a^4(2-a)}{4620}(N-2)(N-3)(N-4)(N-5)(N-6)(33\delta_{J0}+99\delta_{J1}-154\delta_{J2}\\
&\quad -63\delta_{J4}+55\delta_{J5}+30\delta_{J6})F(N-7,J)\Big]\Big\},
\end{aligned}
\tag{2.107}
$$

$$
\begin{aligned}
\langle\hat{n}_p\hat{D}^2+\hat{D}^2\hat{n}_p\rangle_{1,L}=a^2N^3\Big\{&2-a+\frac{3(5-10a+4a^2)}{aN}-\frac{a(-15+28a-11a^2)}{(aN)^2}\\
&+\frac{\bar{L}}{(aN)^2}3(2-a)\Big[1-a+\frac{5-11a+7a^2}{aN}+\frac{2(1-a)(34/3-18a+7a^2)}{(aN)^2}\Big]\\
&-\frac{\bar{L}^2}{(aN)^4}(2-a)\Big[1+\frac{33-71a+60a^2-18a^3}{aN}\Big]\\
&+\frac{\bar{L}^3}{(aN)^6}(2-a)(1-a)(2-2a+a^2)\Big\}.
\end{aligned}
\tag{2.108}
$$

Combining the various expectation values above, and substituting the value of a (2.96) obtained from the VAP procedure, one obtains an analytical expression for the $v=1$ band energies, $E_{1,L}$, similar to Eq. (2.97) for the ground band. This gives a long formula of limited use mainly for numerical comparisons. As it can be easily

reproduced it is not presented here. For purposes of comparison of different bands, the original expressions in terms of a are actually more convenient.

Finally, the equivalent results for the $v = 2$ band are presented. The aim here is to confirm the conjecture made above about the change of structure in neighboring bands. Since the calculations are very laborious to carry out to the third layer, only the second layer results have been obtained. This will be seen to be sufficient for the analysis given here. The expectation values of the one- and two-body operators to the second layer are given by

$$\begin{aligned}\langle \hat{n}_p \rangle_{2,L} = \frac{aN}{2}\Big\{1 + \frac{2-3a}{N} \\ + \frac{\bar{L}}{(aN)^2}(2-a)\Big[1 + \frac{2(5-a)}{aN}\Big] \\ - \frac{\bar{L}^2}{(aN)^4}(2-a)(1-a)\Big\},\end{aligned} \tag{2.109}$$

$$\begin{aligned}\langle \hat{n}_p^2 \rangle_{2,L} = \frac{(aN)^2}{4}\Big\{1 + \frac{14-11a}{aN} + \frac{2(2-9a+6a^2)}{(aN)^2} \\ + \frac{\bar{L}}{(aN)^2}2(2-a)\Big[1 + \frac{7-5a}{aN}\Big] \\ + \frac{\bar{L}^2}{(aN)^4}a(2-a)\Big\},\end{aligned} \tag{2.110}$$

$$\begin{aligned}\langle \hat{D}\cdot\hat{D} \rangle_{2,L} = aN^2\Big\{2 - a + \frac{5-22a+11a^2}{aN} - \frac{4a(1-6a+3a^2)}{(aN)^2} \\ - \frac{\bar{L}}{(aN)^2}(2-a)\Big[2a - 1 - \frac{10(1-a)^2}{aN}\Big] \\ - \frac{\bar{L}^2}{(aN)^4}(2-a)(1-a)^2\Big\}.\end{aligned} \tag{2.111}$$

Eqs. (2.109) and (2.111) reproduce the O(4) results given in Eqs. (A.8) and (A.3), respectively.

The remaining part of this section contrasts the energy expressions obtained for the ground and vibrational bands, and comments on their general features. An immediate observation is that the leading term in each power of $\bar{L}$ (i.e. C_{n0}) is the same in all bands. The next order terms, C_{n1}, which provide the $1/N$ correction to the former, differ from band to band, but the difference between neighboring bands remains constant. That is $C_{n1}(v=1) - C_{n1}(v=0) = C_{n1}(v=2) - C_{n1}(v=1)$. Only in the $1/N^2$ correction terms (C_{n2}), the differences between neighboring bands

vary. For example, for the one- and two-body Hamiltonian (1.12), the second order energy difference describing anharmonicity is given by

$$E_{g,L} - 2E_{1,L} + E_{2,L} = 4\kappa \left[1 - 6a + 3a^2 + \eta_2(2 - 6a + 3a^2)\right]. \tag{2.112}$$

Substituting a from Eq. (2.93), leads to

$$E_{g,L} - 2E_{1,L} + E_{2,L} = \frac{-4\kappa}{1+\eta_2}\left[2 - 3\eta_1^2 + \eta_2(3 - 6\eta_1 - 2\eta_2)\right]. \tag{2.113}$$

Implications of these observations for level energies are as follows; i) vibrational band energies increase linearly with v to leading order, and there are small anharmonic effects of order $1/N$, ii) the MOI of all bands are the same to leading order, and its variation among different bands is of order $1/N$. Both of these features are in accord with experimental systematics, as will be discussed in more detail in Section 2.5.

2.4 Electromagnetic Transitions

In this section, the projected states are used to derive analytic expressions for various electromagnetic transitions, which provide sensitive tests for the wave functions. In contrast to energy levels, transition intensities are not measured very accurately. Therefore, a first layer calculation is usually sufficient in most cases. Reduced matrix elements of a tensor operator $T^{(k)}$ between projected intrinsic states with $K = 0$ are calculated using [5]

$$\langle v', L' \parallel \hat{T}^{(k)} \parallel v, L\rangle = \frac{\hat{L}'(2L+1)}{2[\mathcal{N}(N,v',L')\mathcal{N}(N,v,L)]^{1/2}} \sum_{\mu} \langle L\mu k - \mu | L'0\rangle \times \int_0^{\pi} d\beta \sin\beta d^L_{\mu 0}(\beta) \langle v' | \hat{T}^{(k)}_{-\mu} e^{-i\beta \hat{L}_y} | v\rangle, \tag{2.114}$$

where $\hat{L} = [2L+1]^{1/2}$. Here and in the following, the N quantum number is suppressed since it is a constant.

2.4.1 Infrared Transitions

This section first discusses the inband electric dipole transitions using the one-body operator $\hat{D}$. Applying the boson calculus and projection techniques to Eq. (2.114), gives for transitions in the ground band

$$\langle 0, L' \parallel \hat{D} \parallel 0, L\rangle = N\hat{L}\langle L010|L'0\rangle [a(2-a)]^{1/2} \frac{F(N-1,L) + F(N-1,L')}{2[F(N,L)F(N,L')]^{1/2}}. \tag{2.115}$$

Eq. (2.115) shows that, like in the case of band energies, the transition matrix elements can also be reduced to forms containing the normalization function. Thus, they can be evaluated to any order in $1/N$ using Mathematica. Only the first layer results are presented here, as these are sufficiently accurate for practical purposes

$$\langle 0, L' \parallel \hat{D} \parallel 0, L\rangle = N\hat{L}\langle L010|L'0\rangle[a(2-a)]^{1/2}\Big[1+\frac{1}{N}-\frac{(\bar{L}'-\bar{L})^2}{8(aN)^2}(2a-1)\Big]. \quad (2.116)$$

In obtaining this expression, we have used the relationship $\bar{L}'+\bar{L}=(\bar{L}'-\bar{L})^2/2$ which holds for $L'=L\pm 1$. For $a=1$, Eq. (2.116) reproduces the O(4) result given in Eq. (A.9) to the given order. The final result follows upon substituting the VAP solution for a in (2.116). As the general result is somewhat complicated, we give here the expression for the one-body symmetry breaking with $L'=L+1$

$$\langle 0, L+1 \parallel \hat{D} \parallel 0, L\rangle = N(L+1)^{1/2}(1-\eta_1^2)^{1/2}\Big[1+\frac{1}{N}-\frac{L(L+2)}{2N^2}\frac{1-2\eta_1-\eta_1^2}{(1-\eta_1)^3(1+\eta_1)}\Big]. \quad (2.117)$$

For small perturbations of the O(4) limit, $a_0=1-\sum_i \eta_i$, and the above result can be easily generalized to include other symmetry breaking terms. Inband transition matrix elements in vibrational bands exhibit a similar structure as in the energy expectation values, namely, the leading term in each power of spin remains the same and the $1/N$ corrections vary with bands. Thus, in going from the ground band to the vibrational band v, the only change in Eqs. (2.116) and (2.117) is that the term $1/N$ is replaced by $(1-2v)/N$. The effect of symmetry breaking on inband transitions is seen to be marginal. The change in the leading term in Eq. (2.117) can be absorbed in the dipole charge, and the small change in the $1/N^2$ term does not have any experimental consequence.

The next consideration is the interband transitions which are very sensitive to changes in the vibrational quantum number. For the $\Delta v=1$ transition from the ground band, a calculation similar to Eq. (2.116) yields

$$\langle 1, L' \parallel \hat{D} \parallel 0, L\rangle = \sqrt{N}\hat{L}\langle L010|L'0\rangle(a-1)\Big[1-\frac{1}{2aN}(\bar{L}'-\bar{L}-a)\Big]. \quad (2.118)$$

This expression vanishes in the O(4) limit when $a=1$. For the one-body symmetry breaking with $L'=L+1$, Eq. (2.118) becomes

$$\langle 1, L+1 \parallel \hat{D} \parallel 0, L\rangle = -[N(L+1)]^{1/2}\eta_1\Big[1-\frac{2L+1+\eta_1}{2N(1-\eta_1)}\Big]. \quad (2.119)$$

The corresponding leading order expression for the $\Delta v=2$ transition from the ground band is given by

$$\langle 2, L+1 \parallel \hat{D} \parallel 0, L\rangle = \frac{4\sqrt{2}\eta_1^2(1-\eta_1^2)^{1/2}}{N^2(1-\eta_1)^3}(L+1)^{3/2}. \quad (2.120)$$

Comparing the above matrix elements with those obtained in the mean field theory, Eq. (2.9), it is seen that the leading order results agree as in the case of energies. Projection yields a non-zero result for the $\Delta v = 2$ transition but this is only in the $1/N^2$ term of the series, which is too small to have any practical value. Experimentally, the $v \rightarrow 0$ transitions are 10^v smaller than the ground ones which requires roughly a drop of $N^{v/2}$ in the matrix elements. That is, a leading term of order 1 is needed in Eq. (2.120) to explain the data.

The preceding examples demonstrate that the one-body dipole operator is not sufficient to describe the vibrational transitions even with symmetry breaking. To show the effect of the higher-order terms, the following calculates the same matrix elements with the two-body operator in Eq. (1.23)

$$\langle 0, L+1 \parallel \hat{n}_p\hat{D} + \hat{D}\hat{n}_p \parallel 0, L\rangle = N^2(L+1)^{1/2}[a(2-a)]^{1/2} \times\left[a - \frac{1-a}{N} + \frac{L(L+2)}{2aN^2}(5-4a)\right], \quad (2.121)$$

$$\langle 1, L+1 \parallel \hat{n}_p\hat{D} + \hat{D}\hat{n}_p \parallel 0, L\rangle = N^{3/2}(L+1)^{1/2} \times\left[a(2a-3) + \frac{1}{2N}\Big(2L(1-a) + (4-7a+2a^2)\Big)\right], \quad (2.122)$$

$$\langle 2, L+1 \parallel \hat{n}_p\hat{D} + \hat{D}\hat{n}_p \parallel 0, L\rangle = \sqrt{2}N(L+1)^{1/2}(1-a)\left[1 - \frac{L}{aN}\right]. \quad (2.123)$$

The relative N dependence in the above expressions are now consistent with the data so that one can attempt to use them to describe the dipole transitions among the $v = 0$, 1 and 2 bands. It should be emphasized that the intrinsic matrix element of the two-body operator vanishes for the $3 \rightarrow 0$ transition, and one needs a three-body operator for its description. In general, a v-body operator is required to describe the $v \rightarrow 0$ transition. As suggested in Ref. [8], use of the exponential form (1.24), which includes all the powers of $\hat{n}_p$ in the dipole operator, is the most practical way in dealing with transitions involving higher-vibrational bands. However matrix elements of the operator (1.24) are difficult to evaluate with projection, and therefore are not considered here. Nevertheless, these have been evaluated using mean field theory [8], which is sufficient for practical purposes.

Here, it is of interest to comment on the spin dependent terms in vibrational transitions which arise from rotation-vibration interaction. These terms are represented by Mikhailov plots in collective nuclei and Herman-Wallis forms in molecules. The spin dependent terms in $\Delta v \neq 0$ transitions are seen to vanish in the O(4) limit in all cases, even when the matrix element itself is non-zero. To generate them in the O(4) limit, one needs to include the term $i[\hat{L}\hat{D}' - \hat{D}'\hat{L}]^{(1)}$ in the dipole operator, where $\hat{D}'$ corresponds to the conjugate momentum operator. In the IBM, breaking

of the SU(3) symmetry was shown to provide a natural explanation for spin dependent terms in interband transitions of collective nuclei [25]. Further, these terms exhibit a characteristic $1/N$ dependence as in Eqs. (4.9)-(4.10) (which, incidentally, provide the best signatures for finite N effects in the IBM). The $1/N$ dependence of the slope in Herman-Wallis form gives the right order of magnitude when compared to data. Hence breaking of the O(4) symmetry may explain the spin dependence in vibrational transitions without the need for an extra term in the dipole operator.

2.4.2 Raman Transitions

The available data on Raman transitions are rather scarce, so only a few examples are considered. The ground-band matrix element of the quadrupole operator (1.11) can be reduced to the form

$$\langle 0, L' \parallel \hat{Q} \parallel 0, L\rangle = \frac{\sqrt{5}aN\hat{L}\hat{L}'}{2[F(N,L')F(N,L)]^{1/2}} \times \sum_J \langle 10L'0|J0\rangle\langle L010|J0\rangle \begin{Bmatrix} 1 & L' & J \\ L & 1 & 2 \end{Bmatrix} F(N-1,\ldots,124)$$

where the curly brackets denote the 6-j symbol. The angular momentum algebra in evaluation of Eq. (2.124) is more complicated due to the presence of the 6-j symbol. For the first layer, these are available [5], and one obtains from (2.124)

$$\langle 0, L' \parallel \hat{Q} \parallel 0, L\rangle = \frac{aN}{2}\hat{L}\langle L020|L'0\rangle\left[1 + \frac{a+1}{aN} - \frac{(\bar{L}' - \bar{L})^2}{16aN^2}\right]. \tag{2.125}$$

Substituting $L' = L+2$, L and $L-2$ in Eq. (2.125), expressions for the so called S,O and Q branches in Raman intensities can be obtained. As a final example, the first layer result for the $1 \to 0$ is Raman transition

$$\langle 1, L' \parallel \hat{Q} \parallel 0, L\rangle = \frac{-1}{2}\sqrt{N}\hat{L}\langle L020|L'0\rangle\left[1 - \frac{1}{2aN}(\bar{L}' - \bar{L} - a)\right]. \tag{2.126}$$

Eqs. (2.125) and (2.126) have a similar structure to corresponding matrix elements for infrared transitions, (2.116) and (2.118). Neither expression vanish in the O(4) limit, and therefore, symmetry breaking does not play an important role in these Raman transitions.

2.5 Applications To Molecular Spectra

The analytical $1/N$ expansion formulas derived in the previous sections greatly facilitate systematic study of diatomic molecules in the framework of the vibron

model. As mentioned in the introduction, past applications of the vibron model to molecular spectra have mostly followed the path of the symmetry preserving approach. A primary aim of this study is to assess whether the alternative, symmetry breaking approach can provide a more economical and realistic representation of spectroscopic data. In order to establish a reference point and motivate this study, a comparison of a few key observables in some typical diatomic molecules with the O(4) predictions is made (see Table 2.1). The quantities in Table 2.1 follow from the definitions of the ground and first vibrational band energies as

$$E_{g,L} = C_1\bar{L} + C_2\bar{L}^2 + C_3\bar{L}^3, \quad E_{1,L} = \Delta E + C_1'\bar{L} + C_2'\bar{L}^2 + C_3'\bar{L}^3. \tag{2.127}$$

The other differential quantities are defined as $\Delta C_i = C_i' - C_i$. The data are extracted from the Dunham parameters given in Ref. [26]. The boson numbers are determined from the anharmonicity parameters using the relationship $N + 2 = \omega_e/\omega_e x_e$ [4]. In a few cases where these parameters are not well determined (e.g. AlO and AlS), N appears to be underestimated. While use of a larger N in these cases would have avoided the large fluctuations, leading to a smoother trend in the ratios, this would lead to a rather ad-hoc procedure which has been avoided.

The reasons for the particular way the data are presented are as follows. As stressed before, κ is a scale parameter and it is best determined from the first vibrational energy ΔE. By using ratios of the quantities in Eq. (2.127), this trivial scale parameter is eliminated from the discussions. Secondly, the factors of N are chosen such that the ratios are independent of N. (Only the leading order terms in $1/N$ are considered here. This is sufficient for a qualitative discussion.) Thus the ratios provide universal parameters for description of the spectra of diatomic molecules, independent of the scale parameters. The usefulness of the ratios becomes apparent when one contrasts their range of variation with those of N and C_1. For example, while C_1 (inverse of MOI) varies two orders of magnitude over the range of the molecules presented in Table 2.1, the ratio $N\Delta C_1/C_1$ remains practically constant. Below, the experimental systematics for each ratio are discussed and contrasted with the O(4) predictions.

(a) $\Delta E/NC_1$; ΔE and C_1 are the two most important spectroscopic quantities characterizing the vibrational and rotational excitations, respectively. When $\kappa' = 0$, the O(4) limit has the parameter free prediction of 4 for this ratio, which is smaller than the observed values listed in Table 2.1. The halides are the closest to the O(4) value with some 10-30% deviation, but as one moves to heavier and more symmetric molecules, the difference becomes a factor of 2-3. Clearly one needs a smaller C_1 (larger MOI) than predicted by the O(4) limit. An easy way to achieve this is to introduce the $\hat{L}\cdot\hat{L}$ term in the Hamiltonian with a negative κ'. But as stressed

Table 2.1: Experimental values for the ratios considered in Section 2.5. The data are from Ref. [26] and listed in order of increasing MOI. The O(4) values (with $\kappa' = 0$) are shown at the top row for reference. C_1 is in cm^{-1}.

Molecule	N	C_1	$\Delta E/NC_1$	N^2C_2/C_1	N^4C_3/C_1	$N\Delta C_1/C_1$	$N\Delta C_2/C_2$
O(4)		κ	4.00	0	0	0	-
$^{1}H\,^{19}F$	44	20.6	4.38	-0.200	0.029	-1.65	-1.2
$^{1}H\,^{35}Cl$	55	10.1	5.17	-0.158		-1.60	-0.70
$^{1}H\,^{81}Br$	57	8.35	5.38	-0.134	0.010	-1.58	-0.51
$^{12}C\,^{16}O$	161	1.92	6.92	-0.0825	0.002	-1.51	
$^{9}Be\,^{16}O$	124	1.64	7.19	-0.0768	0.002	-1.44	-0.15
$^{32}S\,^{16}O$	202	0.718	7.85	-0.0642		-1.69	
$^{27}Al\,^{16}O$	138	0.638	11.0	-0.0325		-1.30	2.5
$^{27}Al\,^{19}F$	166	0.550	8.68	-0.0526		-1.51	-0.24
$^{27}Al\,^{32}S$	183	0.279	12.0	-0.0264		-1.31	
$^{27}Al\,^{35}Cl$	245	0.243	8.02	-0.0618	-0.001	-2.02	-0.52
$^{27}Al\,^{79}Br$	293	0.158	8.11	-0.0613	-0.001	-1.85	-0.52

earlier, this is an artificial way to increase the MOI because it does not lead to a corresponding increase in molecular size. A better and physically more appealing way would be to break the O(4) limit in such a way that the size parameter r (or a) gets larger than the O(4) value of 1 as the MOI increases.
(b) N^2C_2/C_1; This ratio measures the softness of a rotor, that is the ability of a molecule to stretch while it rotates faster and faster in the ground band. The experimental values in Table 2.1 cover a wide range, from -0.2 in the halides to -0.02 in AlS. It vanishes in the O(4) limit, which corresponds to a rigid rotor. But as seen in Section 2.3, any breaking of the O(4) limit leads to non-zero values for this ratio, and hence they could provide a more natural explanation for the softness parameter than including the term $(\hat{L}\cdot\hat{L})^2$ in the Hamiltonian.
(c) N^4C_3/C_1; This ratio provides a correction to the softness at high spins, and it is usually positive. Again it vanishes in the O(4) limit. One can accommodate the experimental values by either breaking the O(4) limit or including $(\hat{L}\cdot\hat{L})^3$ term in the Hamiltonian.
(d) $N\Delta C_1/C_1$; The differential change in C_1 as depicted by this ratio remains remarkably constant for the diatomic molecules listed in Table 2.1. The negative sign reflects the fact that the MOI of the molecules gets larger with increasing vibrational number. In the O(4) limit, all the bands have the same MOI, hence this ratio vanishes. The observed changes in MOI can be reproduced by either including the quartic term $\hat{D}\cdot\hat{D}\,\hat{L}\cdot\hat{L}$ in the Hamiltonian or more generally, by breaking the O(4) limit.
(e) $N\Delta C_2/C_2$; This is similar to (d) above but for the softness parameter C_2. The experimental values show more variation but are generally negative (except AlO). It is indeterminate in the O(4) limit as $C_2 = 0$ for all bands.
As stressed earlier, the change in band structure is linear (to leading order) for low-lying bands, therefore the above quantities provide a good overall representation for the spectroscopic data.

2.5.1 Minimal Breaking of O(4)

Taking the simplest case first, this section first considers a minimal breaking of the O(4) limit via the Hamiltonian (1.12). The effect of the $\hat{n}_p$ and $\hat{n}_p^2$ terms on the ratios (a) to (e) introduced above are shown in Figs. 2.1- 2.5. In each figure, a particular ratio is plotted against the parameter η_1 for various values of η_2. Both parameters are varied in the range of $[-0.3, 0.3]$, η_1 continuously and η_2 in steps of 0.1. Fig. 2.1, shows the effect of the symmetry breaking on the ratio $\Delta E/NC_1$, which is seen to be coherent for η_1 and η_2. That is, they both reduce this ratio

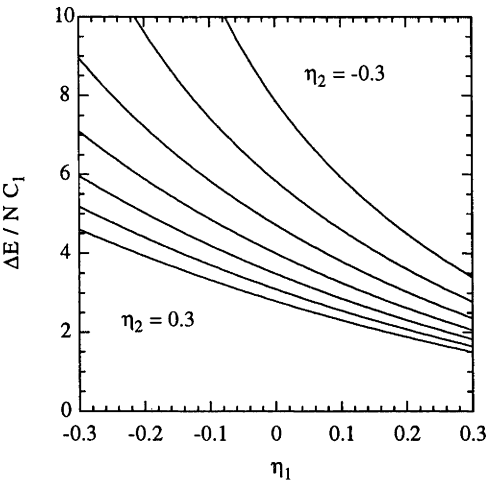

Figure 2.1: The effect of the one- and two-body symmetry breaking terms with strength parameters η_1 and η_2 on the ratio $\Delta E/NC_1$. The parameter η_2 is varied from -0.3 to 0.3 in steps of 0.1

from its O(4) value of 4 for positive values, and conversely, increase it for negative values. The latter range is preferred by the experimental values quoted in Table 2.1, which require a larger MOI than that provided by the dipole interaction alone. Note that for negative η_1 or η_2, a (or r) gets larger than the O(4) value (see Eq. (2.90)). Thus the increase in MOI is associated with a corresponding increase in molecular size. Note that the situation in the IBM description of deformed nuclei is exactly the opposite, namely, the dominant quadrupole-quadrupole interaction there leads to a too large MOI that needs to be reduced by addition of (positive) one-body energies [27]. This choice of sign in the IBM has firm microscopic foundations in the pairing property of the nucleon-nucleon interaction. In the case of diatomic molecules, there is no microscopic basis for the bosons, and the choice of sign for the symmetry breaking terms is purely motivated by phenomenology.

Figures 2.2 and 2.3 show the variation of the ground-band MOI with spin. The two ratios N^2C_2/C_1 and N^4C_3/C_1, which measure the deviation from the rigid-rotor behaviour, are plotted in Figs. 2.2 and 2.3, respectively. Symmetry breaking by η_1 gives the correct sign for N^2C_2/C_1 but the magnitude is not large enough to accommodate the observed values, especially for the halides. The positive range of η_2 lead to the wrong sign, thus they are excluded by this set of data. The negative range of η_2, on the other hand, give the correct sign and they are much more effective than η_1 in reproducing the experimental range. The ratio N^4C_3/C_1 has the wrong

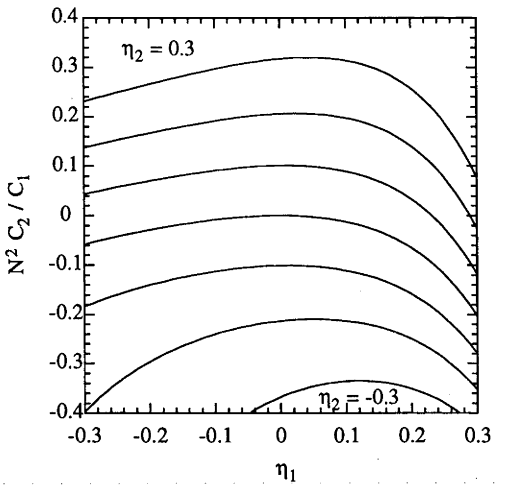

Figure 2.2: The effect of the one- and two-body symmetry breaking terms with strength parameters η_1 and η_2 on the ratio N^2C_2/C_1. The parameter η_2 is varied from -0.3 to 0.3 in steps of 0.1.

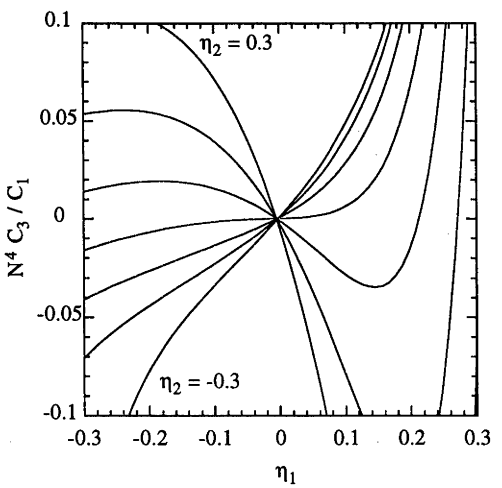

Figure 2.3: The effect of the one- and two-body symmetry breaking terms with strength parameters η_1 and η_2 on the ratio N^4C_3/C_1. The parameter η_2 is varied from -0.3 to 0.3 in steps of 0.1.

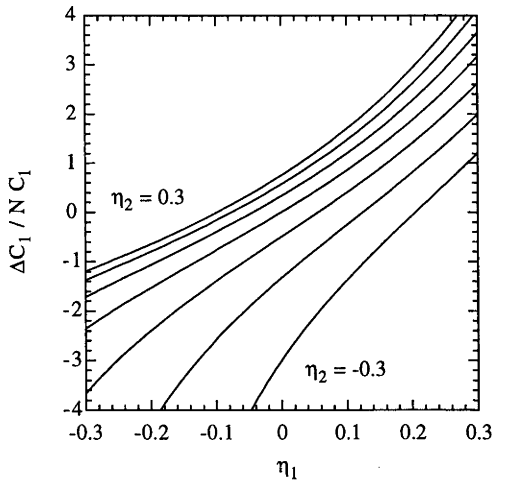

Figure 2.4: The effect of the one- and two-body symmetry breaking terms with strength parameters η_1 and η_2 on the ratio $N\Delta C_1/C_1$. The parameter η_2 is varied from -0.3 to 0.3 in steps of 0.1 .

sign in most cases when both η_1 and η_2 are negative. Nevertheless, a small positive η_1 and a larger negative η_2 could still explain all three ratios discussed so far.

The change in MOI among different bands is illustrated in Figures 2.4 and 2.5. The ratios $N\Delta C_1/C_1$ and $N\Delta C_2/C_2$ are plotted in Figures 2.4 and 2.5 respectively. The former can be described by a band values satisfying $\eta_1 + \eta_2 \approx -0.2$, which is still consistent with the previous ratios. But the latter ratio, which is indeterminate in the O(4) limit, exhibits large variations far outside the experimental range for any value of the symmetry breaking terms. Explanation of this ratio calls for higher order terms in the Hamiltonian.

As already mentioned in Section 2.4, the one-body dipole operator is not sufficient to describe the infrared transitions beyond $\Delta v = 1$. Here we discuss the case of $\Delta v = 1$ dipole transitions, where symmetry breaking provides the right order of magnitude as far as the N dependence is concerned. From Eqs. (2.119) and (2.117) the ratio of $1 \rightarrow 0$ to $0 \rightarrow 0$ transition is roughly given by $\eta_1/\sqrt{N}$. Since the dynamic considerations above limits the values η to about %20, symmetry breaking could provide only a fraction of the experimental ratio. This again underscores the importance of higher-order terms in the transition operator.

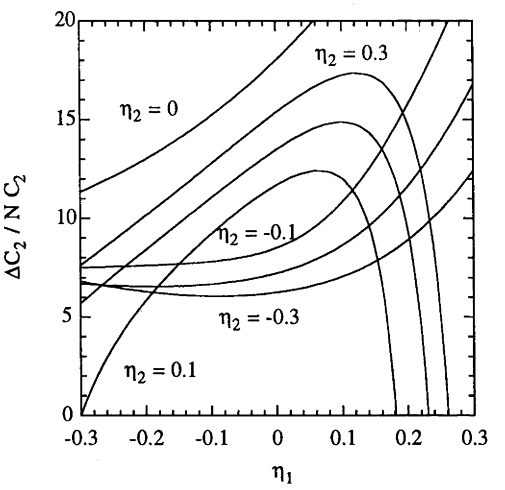

Figure 2.5: The effect of the one- and two-body symmetry breaking terms with strength parameters η_1 and η_2 on the ratio $N\Delta C_2/C_2$. The parameter η_2 is varied from -0.3 to 0.3 in steps of 0.1 .

2.5.2 Higher Order Terms

This section discusses the symmetry breaking due to the higher order terms, namely, three-body interactions in the Hamiltonian and two-body terms in the dipole transition operator. The effect of the three cubic terms on the ratios (a) to (e) are shown in Figs. 2.6-2.10. The presentation is similar to Figs. 2.1-2.5 with η_2 being replaced by η_3 in (a), η_3' in (b) and η_3'' in (c) of each figure. The effect of the cubic terms on the ratio $\Delta E/NC_1$ is shown in Fig. 2.6. The curves in Fig. 2.6 exhibit broadly similar features as in the case of η_2 in Fig. 2.1, thus the same comments apply here. In details, η_3' dependence is more uniform and weaker compared to the others .

Fig. 2.7 studies the dependence of the ratio N^2C_2/C_1 on the cubic terms. Again, the curves in Fig. 2.7 exhibit similar patterns as in Fig. 2.2 showing the η_2 dependence. Two important differences are that η_3 is even more effective than η_2 in inducing changes in this ratio, and the sign dependence for η_3' is reversed compared to the others. These features would be helpful in fine tuning of the parameters. Fig. 2.8 repeats the same study for the ratio N^4C_3/C_1. In this case, there are no common features among different figures. Noteworthy is the η_3 dependence, which is very sensitive to this ratio, and hence η_3 would be best determined by fits to the C_3 coefficient of the ground-band MOI.

The variation in MOI with bands is studied in Figs. 2.9 and 2.10. In Fig. 2.9, the dependence of the ratio $N\Delta C_1/C_1$ on the cubic terms is seen to be similar to that of η_2 in Fig. 2.4 but much weaker in its effect. Thus this ratio should be fitted by the η_1 and η_2 parameters. The unstable nature of the ratio $N\Delta C_2/C_2$ encountered in Fig. 2.5 is cured by the addition of the cubic terms (Fig. 2.10). The η_3 range are still outside the experimental range but the other two could explain the data. Clearly, in order to reproduce this ratio, one has to balance the cubic parameters carefully.

Inclusion of the two-body term in the dipole operator clearly cures the problem in the $\Delta v = 1$ transitions mentioned above. From Eqs. (4.9) and (4.8), the $1 \rightarrow 0/1 \rightarrow 0$ ratio is given by $1/\sqrt{N}$, consistent with the data. However, the same ratio for the $\Delta v = 2$ transition is still proportional to η, hence it suffers from the same problem. This again can be resolved by either including the three-body term in (1.23), or, more practically, using the exponential form (1.24).

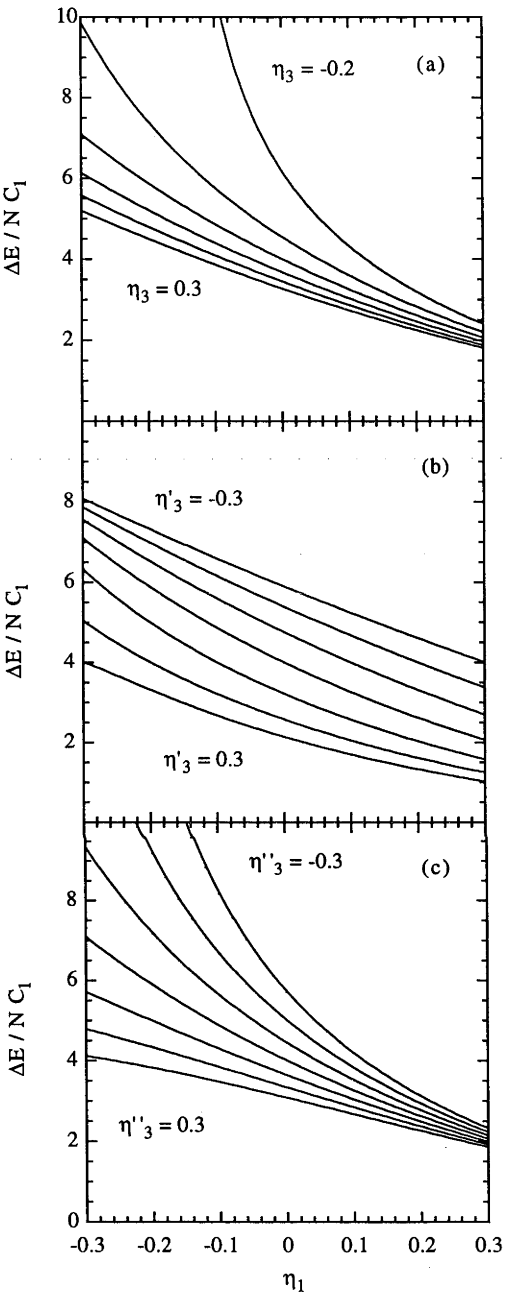

Figure 2.6: The effect of the cubic terms with strength parameters η_3, η_3' and η_3'' on the ratio $\Delta E/NC_1$. The parameters are varied from -0.3 to 0.3 in steps of 0.1, except for η_3 which is varied from -0.1 to 0.3. Lower η_3 values are excluded because they lead to excessive fluctuations in the graphs.

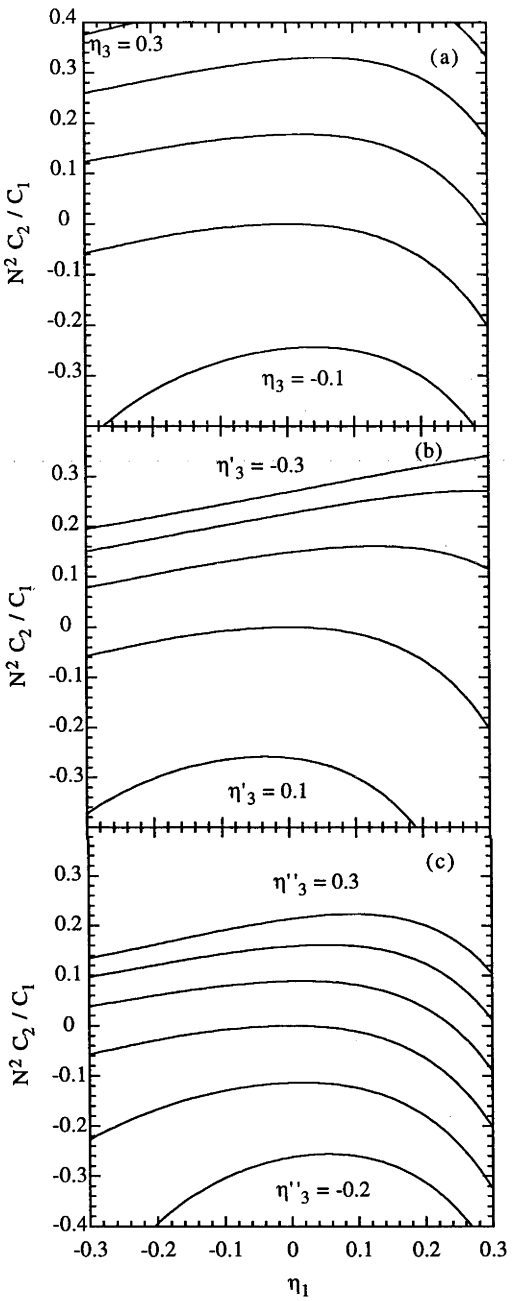

Figure 2.7: The effect of the cubic terms with strength parameters η_3, η'_3 and η''_3 on the ratio N^2C_2/C_1. The parameters are varied from -0.3 to 0.3 in steps of 0.1, except for η_3 which is varied from -0.1 to 0.3. Lower η_3 values are excluded because they lead to excessive fluctuations in the graphs.

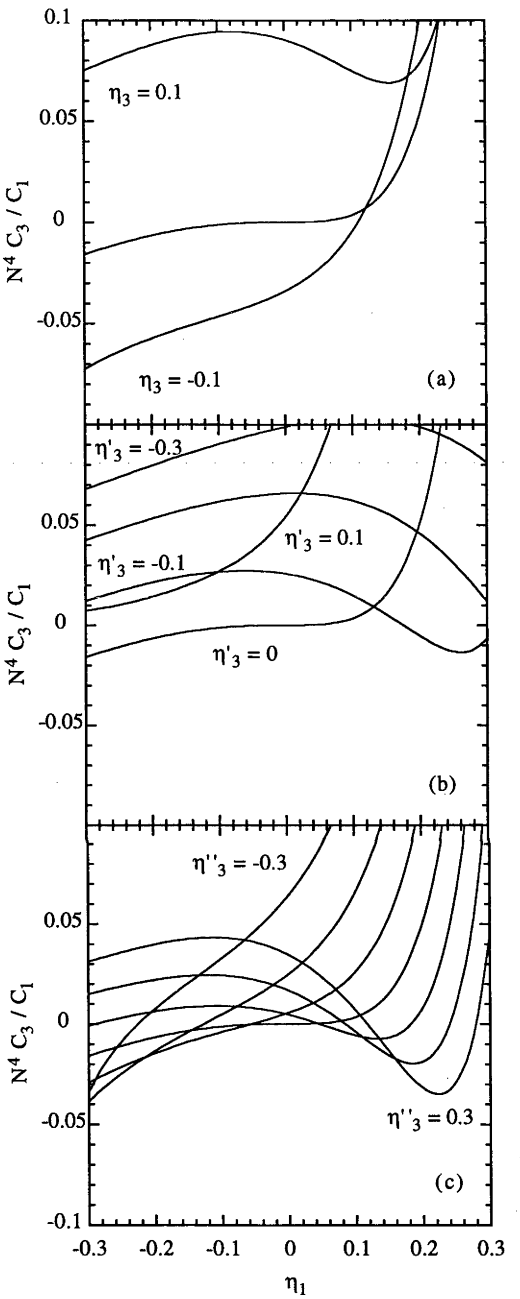

Figure 2.8: The effect of the cubic terms with strength parameters η_3, η'_3 and η''_3 on the ratio N^4C_3/C_1. The parameters are varied from -0.3 to 0.3 in steps of 0.1, except for η_3 which is varied from -0.1 to 0.3. Lower η_3 values are excluded because they lead to excessive fluctuations in the graphs.

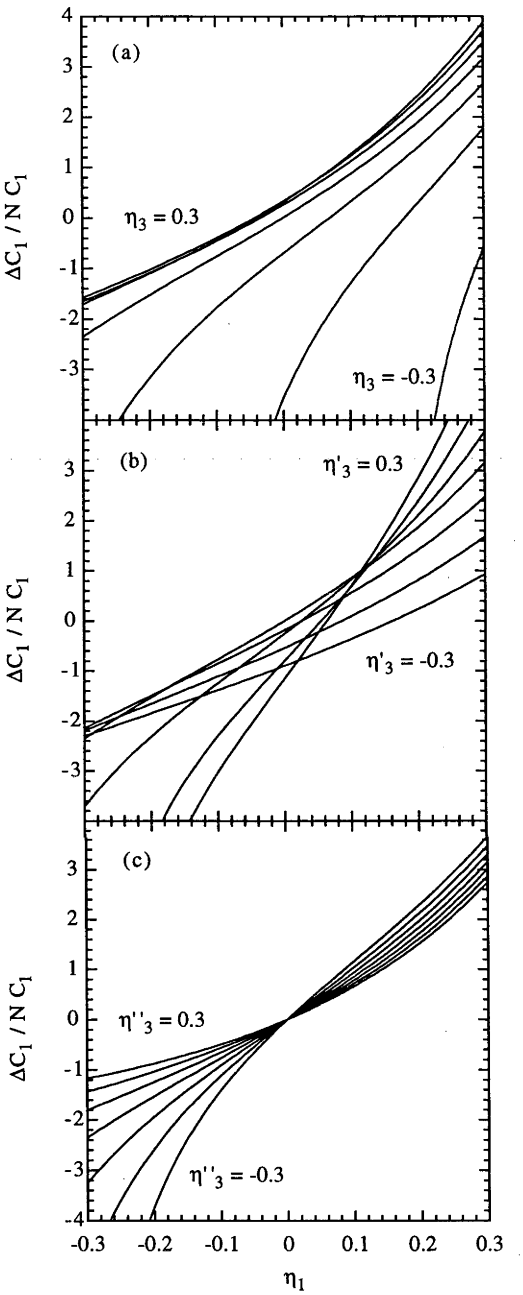

Figure 2.9: The effect of the cubic terms with strength parameters η_3, η_3' and η_3'' on the ratio $N\Delta C_1/C_1$. The parameters are varied from -0.3 to 0.3 in steps of 0.1, except for η_3 which is varied from -0.1 to 0.3. Lower η_3 values are excluded because they lead to excessive fluctuations in the graphs.

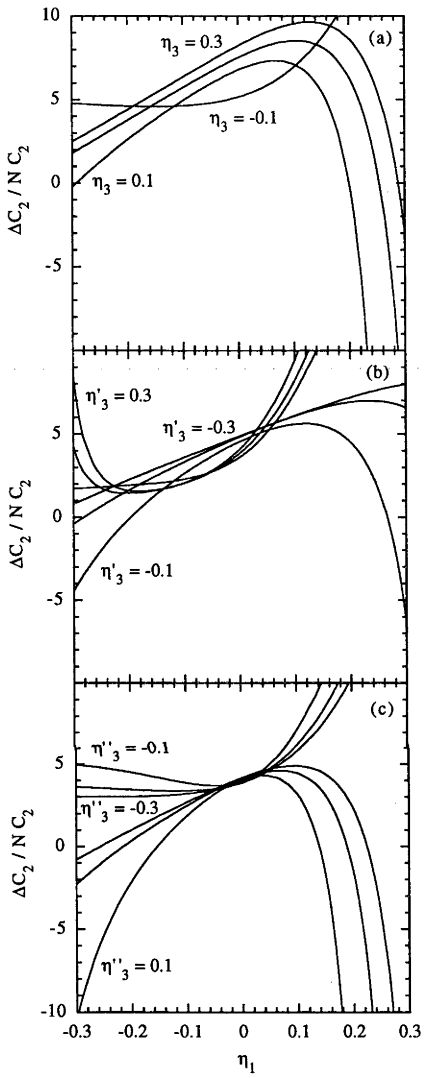

Figure 2.10: The effect of the cubic terms with strength parameters η_3, η'_3 and η''_3 on the ratio $N\Delta C_2/C_2$. The parameters are varied from -0.3 to 0.3 in steps of 0.1, except for η_3 which is varied from -0.1 to 0.3. Lower η_3 values are excluded because they lead to excessive fluctuations in the graphs. The curves for $\eta_3 = 0$, $\eta'_3 = 0$, and $\eta''_3 = 0$ lie outside the figures (cf. Fig. 2.5).

CHAPTER 3

Triatomic Molecules

In this chapter, the $1/N$ expansion formalism is extended to linear triatomic molecules. Since axial symmetry is preserved in linear molecules, this extension is conceptually straightforward, only that it entails more complex calculations. Bent molecules are not considered in this work because they require projection from a non-axial intrinsic state, which is a rather difficult problem to tackle with analytical methods. In the first section, mean field theory of triatomic molecules is reviewed, and solutions to the variational problem are discussed. In the second section, the projected normalization is evaluated using the improved Gaussian approximation. In the following sections, energy expressions for the ground-band and first overtones are derived, and applied to selected data in triatomic molecules.

3.1 Mean Field Theory

This section presents a general mean field study of the one- and two-body Hamiltonian introduced in Eqs. (1.29-1.31). One purpose of this study is to determine the range of parameters that lead to linear molecules. This is necessary to ensure that the applications of the $1/N$ expansion results derived under the assumption of linear molecules remain within those boundaries. For triatomic molecules the variational ground-state band is given by the product of the individual coherent states

$$|N_1, N_2, r_1, r_2\rangle = (N_1 N_2)!(b_1^\dagger)^{N_1}(b_2^\dagger)^{N_2}|0\rangle. \tag{3.1}$$

In general axial symmetry is lost so that, aligning the 'second' bond along the z axis, the intrinsic bosons may be expressed as

$$\begin{aligned} b_1^\dagger &= (1+r_1^2)^{-1/2}(s_1^\dagger + \mathbf{r}_1 \cdot \mathbf{p}_1^\dagger), \\ &= (1+r_1^2)^{-1/2}\left(s_1^\dagger + r_1(\cos\theta p_{10}^\dagger + \frac{1}{\sqrt{2}}\sin\theta p_{1-1}^\dagger - \frac{1}{\sqrt{2}}\sin\theta p_{11}^\dagger)\right), \\ b_2^\dagger &= (1+r_2^2)^{-1/2}(s_2^\dagger + r_2 p_{20}^\dagger). \end{aligned} \tag{3.2}$$

where r_1 and r_2 are the two variational parameters associated with the two interatomic distances and θ is a further variational parameter describing the angle between the bonds.

For a given triatomic Hamiltonian H, the energy surface is determined from

$$E(r_1, r_2, \theta) = \langle N_1, N_2, r_1, r_2 | H | N_1, N_2, r_1, r_2 \rangle. \tag{3.3}$$

For the Hamiltonian in Eqs. (1.29-1.31), this leads to the expression

$$\begin{aligned} E(r_1, r_2, \theta) &= \sum_{i=1}^{2} \left[-4\kappa_i N_i^2 \left(\frac{r_i}{1+r_i^2} \right)^2 + \varepsilon_i N_i \frac{r_i}{1+r_i^2} + \sigma_i N_i^2 \left(\frac{r_i^2}{1+r_i^2} \right)^2 \right] \\ &+ \frac{N_1 N_2}{(1+r_1^2)(1+r_2^2)} \Big[(-4\kappa_{12} r_1 r_2 \cos\theta + \sigma_{12} r_1^2 r_2^2) \\ &+ \lambda_4 (r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta) + (\lambda_3 + \lambda_4)(r_1 r_2 \sin\theta)^2 \Big]. \end{aligned} \tag{3.4}$$

The variational parameters are then obtained from the extremum conditions

$$\begin{aligned} \frac{\partial E(r_1, r_2, \theta)}{\partial r_i} &= 0, \\ \frac{\partial E(r_1, r_2, \theta)}{\partial \theta} &= 0. \end{aligned} \tag{3.5}$$

The energy surface (3.4) had been obtained previously in Refs. [12] and [17], but its variational solution was not discussed in any detail. Because of the rational form, variation of $E(r_1, r_2, \theta)$ is somewhat complicated. This takes a more amenable form using the variable

$$a_i = \frac{2 r_i^2}{1 + r_i^2}, \quad i = 1, 2, \tag{3.6}$$

which was introduced in the diatomic case because of its convenience. After this transformation, the energy surface becomes

$$\begin{aligned} E(a_1, a_2, \theta) &= \sum_{i=1}^{2} N_i^2 \Big[-\kappa_i a_i (2 - a_i) + \frac{1}{2} \varepsilon_i' a_i + \frac{1}{4} \sigma a_i^2 \Big] \\ &+ N_1 N_2 \Big[\frac{1}{4} \sigma_{12} a_1 a_2 + \frac{1}{2} \lambda_4 (a_1 + a_2 - a_1 a_2) \\ &- \frac{1}{2} (2\kappa_{12} + \lambda_4) [a_1 (2 - a_1) a_2 (2 - a_2)]^{1/2} \cos\theta \\ &+ \frac{1}{4} (\lambda_3 + \lambda_4) a_1 a_2 \sin^2\theta \Big]. \end{aligned} \tag{3.7}$$

where $\varepsilon_i' = \varepsilon_i / N_i$. The variational parameters are then determined from the extremum conditions, by setting the following derivatives to zero

$$\frac{\partial E(a_1, a_2, \theta)}{\partial a_1} = -2\kappa_1 N_1^2 (1 - a_1) + \frac{1}{2} \varepsilon_1' N_1^2 + \frac{1}{2} \sigma_1 N_1^2 a_1 + \frac{1}{4} \sigma_{12} N_1 N_2 a_2$$

$$+\frac{1}{2}\lambda_4 N_1 N_2(1-a_2) - \frac{1}{2}N_1 N_2(2\kappa_{12}+\lambda_4)(1-a_1)\left[\frac{a_2(2-a_2)}{a_1(2-a_1)}\right]^{1/2}\cos\theta$$
$$+\frac{1}{4}(\lambda_3+\lambda_4)N_1 N_2 a_2 \sin^2\theta, \tag{3.8}$$

$$\frac{\partial E(a_1,a_2,\theta)}{\partial a_2} = -2\kappa_2 N_2^2(1-a_2)+\frac{1}{2}\varepsilon_2' N_2^2+\frac{1}{2}\sigma_2 N_2^2 a_1+\frac{1}{4}\sigma_{12}N_1 N_2 a_1$$
$$+\frac{1}{2}\lambda_4 N_1 N_2(1-a_1) - \frac{1}{2}N_1 N_2(2\kappa_{12}+\lambda_4)(1-a_2)\left[\frac{a_1(2-a_1)}{a_2(2-a_2)}\right]^{1/2}\cos\theta$$
$$+\frac{1}{4}(\lambda_3+\lambda_4)N_1 N_2 a_1 \sin^2\theta, \tag{3.9}$$

$$\frac{\partial E(a_1,a_2,\theta)}{\partial \theta} = \frac{1}{2}N_1 N_2 \sin\theta\Big[(2\kappa_{12}+\lambda_4)[a_1(2-a_1)a_2(2-a_2)]^{1/2}\cos\theta$$
$$+\frac{1}{4}(\lambda_3+\lambda_4)a_1 a_2\cos\theta\Big]. \tag{3.10}$$

Eq. (3.10) has 3 solutions for the variable θ, given by $\theta = 0, \pi$ and

$$\cos\theta = -\frac{2\kappa_{12}+\lambda_4}{\lambda_3+\lambda_4}\left[\frac{(2-a_1)(2-a_2)}{a_1 a_2}\right]^{1/2}. \tag{3.11}$$

These three solutions are considered separately below.

i) $\theta = 0$: Substituting $\theta = 0$ in Eqs. (3.8) and (3.9), and setting each equal to zero, one obtains

$$-N_1(4\kappa+\sigma_1)a_1 + N_2(\sigma_{12}/2-\lambda_4)a_2 + (-4N_1\kappa_1 + N_1\varepsilon_1' + N_2\lambda_4) = N_2\gamma(1-a_1)\left[\frac{a_2(2-a_2)}{a_1(2-a_1)}\right]^{-1/2}, \tag{3.12}$$

$$-N_2(4\kappa+\sigma_2)a_2 + N_1(\sigma_{12}/2-\lambda_4)a_1 + (-4N_2\kappa_2 + N_2\varepsilon_2' + N_1\lambda_4) = N_1\gamma(1-a_2)\left[\frac{a_1(2-a_1)}{a_2(2-a_2)}\right]^{-1/2}, \tag{3.13}$$

where $\gamma = 2\kappa_{12}+\lambda_4$. From the study of diatomic molecules, it is expected that a_i remains near one for small perturbations of the $O(4)$-like dynamical symmetries. Thus, as a first approximation, one can replace the square root terms above with one. The solutions of the resulting linear equations are then given by

$$a_1 = \frac{[N_1(4\kappa_1-\varepsilon_1')+2N_2\kappa_{12}][N_2(4\kappa_2+\sigma_2)+N_1\gamma]-N_2^2(4\kappa_2-\varepsilon_2')(\sigma_{12}/2-\lambda_4)}{[N_1(4\kappa_1+\sigma_1)+N_2\gamma][N_2(4\kappa_2+\sigma_2)+N_1\gamma]-N_1N_2(\sigma_{12}/2-\lambda_4)^2}, \tag{3.14}$$

$$a_2 = \frac{[N_2(4\kappa_2-\varepsilon_2')+2N_1\kappa_{12}][N_1(4\kappa_1+\sigma_1)+N_2\gamma]-N_1^2(4\kappa_1-\varepsilon_1')(\sigma_{12}/2-\lambda_4)}{[N_1(4\kappa_1+\sigma_1)+N_2\gamma][N_2(4\kappa_2+\sigma_2)+N_1\gamma]-N_1N_2(\sigma_{12}/2-\lambda_4)^2}. \tag{3.15}$$

If required, these can be improved by iterating the solutions. Notice that the square root factors in Eqs. (3.12-3.13) are multiplied by γ. Thus, to iterate, one can simply multiply γ in the above solutions with the square root factors obtained by substituting the approximate a_i values from the previous iteration.
ii) $\theta = \pi$: The solutions in this case are given by those in (i) above upon substituting $\gamma \rightarrow -\gamma$.
iii) The third solution for θ is rather complicated. Since numerical studies indicate that it does not lead to an absolute minimum of energy surface for small perturbations of dynamical symmetries, it is not considered here.

For X_2Y molecules, the solutions are considerably simplified, and they could provide more insight. Substituting $a_1 = a_2 = a$ and similarly setting all the other single boson Hamiltonian parameters equal gives for the energy surface

$$\begin{aligned} E(a,\theta) &= \frac{1}{2}N^2\Big[-4\kappa a(2-a) + 2\varepsilon' a + (\sigma + \sigma_{12}/2)a^2 - 2\kappa_{12}a(2-a)\cos\theta \\ &\quad +\lambda_4 a(2-a)(1-\cos\theta) + \frac{1}{2}(\lambda_3+\lambda_4)a^2\sin^2\theta\Big]. \end{aligned} \tag{3.16}$$

Note that the number of variational parameters to be considered is reduced to two and there are no complicating square root factors. As in the more general case, there are three possible solutions for θ, which are examined in turn.
i) $\theta = 0$: the solution for a is

$$a = \frac{4\kappa + 2\kappa_{12} - \varepsilon'}{4\kappa + 2\kappa_{12} + \sigma + \sigma_{12}/2}, \tag{3.17}$$

and the corresponding energy is

$$E(\theta = 0) = -\frac{N^2(4\kappa + 2\kappa_{12} - \varepsilon')^2}{8\kappa + 4\kappa_{12} + 2\sigma + \sigma_{12}}. \tag{3.18}$$

Note that in this instance there is no dependence on the Majorana operators.
ii) $\theta = \pi$: the solution for a is

$$a = \frac{4\kappa - 2\kappa_{12} - 2\lambda_4 - \varepsilon'}{4\kappa - 2\kappa_{12} - 2\lambda_4 + \sigma + \sigma_{12}/2}, \tag{3.19}$$

giving the energy solution

$$E(\theta = \pi) = -\frac{N^2(4\kappa - 2\kappa_{12} - 2\lambda_4 - \varepsilon')^2}{8\kappa - 4\kappa_{12} - 4\lambda_4 + 2\sigma + \sigma_{12}}. \tag{3.20}$$

The difference from (i) are that it has a dependence on λ_4 and the sign of κ_{12} term is opposite. Given the the usual positive values of these parameters, then (i) would result in a lower energy.

iii) The third solution would correspond to a bent molecule with the bond angle determined by

$$\cos\theta = -\frac{(2\kappa_{12}+\lambda_4)(2-a)}{(\lambda_3+\lambda_4)a}, \tag{3.21}$$

In this case, the solution for a is given by

$$a = 2\frac{(2\kappa_{12}+\lambda_4)^2+(4\kappa-\varepsilon'-\lambda_4)(\lambda_3+\lambda_4)}{(2\kappa_{12}+\lambda_4)^2+(8\kappa+2\sigma+\sigma_{12}+\lambda_3-\lambda_4)(\lambda_3+\lambda_4)}, \tag{3.22}$$

and substituting this result in Eq. (3.21), the θ solution becomes

$$\cos\theta = -\frac{(2\kappa_{12}+\lambda_4)(4\kappa+\varepsilon'+2\sigma+\sigma_{12}+\lambda_3)}{(2\kappa_{12}+\lambda_4)^2+(4\kappa-\varepsilon'-\lambda_4)(\lambda_3+\lambda_4)}. \tag{3.23}$$

Finally, the energy is

$$E_\theta = -N^2\left[\frac{(4\kappa-\varepsilon'-\lambda_4)^2(\lambda_3+\lambda_4)-(2\kappa_{12}+\lambda_4)^2(\lambda_3+\lambda_4+2\varepsilon'+2\sigma+\sigma_{12})}{(2\kappa_{12}+\lambda_4)^2+(8\kappa+2\sigma+\sigma_{12}+\lambda_3-\lambda_4)(\lambda_3+\lambda_4)}\right]. \tag{3.24}$$

Note that at all times in the above analysis $2\sigma+\sigma_{12}$ may be trivially replaced by σ', which simplifies consideration of the effect of these symmetry breaking terms.

A numerical analysis of the three energy extrema obtained above indicates that the bending solution is bracketed by the other two for small perturbations of the dynamical symmetries, hence such Hamiltonians can only describe linear triatomic molecules.

3.2 Polyatomic Normalization

As described in the last section, coherent states for the extended SGA are simply given by the product of individual coherent states. Unfortunately, the methods described in [22] for the evaluation of the projection integrals do not work for products of coherent states. A Gaussian approximation can be invoked to get around this difficulty [5]. However, this limits the accuracy of the expansion to order $1/N$, which is not good enough for practical applications of the method. (It has been demonstrated in the last chapter that the accuracy of the $1/N$ expansion solutions depends directly on how accurately one can evaluate the projected normalization integral for coherent states.) Description of polyatomic molecules in the vibron model are then limited to leading order terms in band energies, moment of inertia and electric dipole transitions. Part of the interesting physics in molecular spectroscopy derives from the $1/N$ correction terms to these quantities, which cannot be obtained accurately using the Gaussian approximation. Thus, for the $1/N$ expansion to be useful in applications to the extended SGA, it is essential to find a

method whereby one can evaluate the projected norm integral to a desired level of accuracy.

In Appendix B, a new method for evaluating angular momentum projected integrals, based on an improvement of the Gaussian approximation, is demonstrated for a single-boson system. This section generalizes this method to multi-boson systems, and expressions for the norm integral, accurate to high orders in $1/N$, are derived. This result forms the basis for the triatomic energy calculations to be presented in the following sections. The derivation is given for a general multi-boson system with axial symmetry, so that the results can be applied to other bosonic SGA. In particular, they will be useful in improving the previous $1/N$ expansion results for the proton-neutron IBM [5].

For a system of bosons described by the SGA $\mathrm{U}_1 \otimes \mathrm{U}_2 \otimes \ldots \otimes \mathrm{U}_n$, there are n types of orthogonal bosons, which are collectively denoted by the set of operators $\{b^\dagger_{ilm}, b_{ilm}, i = 1, 2, \ldots, n\}$. Assuming that the ground state of this boson system is axially symmetric, it can be written as a product of individual coherent states

$$|N_1, \mathbf{x}_1, N_2, \mathbf{x}_2, \ldots, N_n, \mathbf{x}_n\rangle = \prod_{i=1}^{n} (N_i!)^{-1/2} \left(b^\dagger_i\right)^{N_i} |0\rangle, \quad b^\dagger_i = \sum_l x_{il} b^\dagger_{il0}. \tag{3.25}$$

The norm of the intrinsic state (3.25) with angular momentum projection is given by

$$\mathcal{N}_g(N_1, N_2, \ldots, N_n, L) = \frac{2L+1}{2} \int_0^\pi d\beta \sin\beta \, P_L(\beta) \prod_{i=1}^{n} [Z_i(\beta)]^{N_i}, \tag{3.26}$$

where Z_i are defined as in (2.20) with $x_l \to x_{il}$. For each $Z_i^{N_i}$ in (3.26), the ansatz (B.4) is used with the substitutions $N \to N_i$, $a_n \to a_{in}$ and $c_k \to c_{ik}$. Here a_{in} are defined by Eq. (C.5), with $x_l \to x_{il}$, and the solutions for c_{ik} follow from Eq. (B.7) with the above substitutions for N and a_n. With these definitions, the improved Gaussian integral for (3.26) can be written as

$$I = \int_0^\infty d\beta \sin\beta \, P_L(\beta) \exp[-\bar{a}N\beta^2/4] \prod_{i=1}^{n} \Big(1 + \sum_{k=4,6,} c_{ik}\beta^k\Big), \tag{3.27}$$

introducing the average $\bar{a}$ as

$$\bar{a}N = \sum_{i=1}^{n} a_i N_i, \quad N = \sum_{i=1}^{n} N_i. \tag{3.28}$$

When all $c_{ik} = 0$ (i.e. the Gaussian approximation), the integral (3.27) reduces to the same form as for the single-coherent state (B.2). Thus, with the above definition for $\bar{a}N$, the Gaussian approximation leads exactly to the same $1/N$ expansion for the multi-boson systems as in the single-boson case, that is, Eq. (2.27) with the

coefficients α_{nm} given in Eq. (B.3). This equivalence of the Gaussian approximations in form is very important in generalizing the method to multi-boson systems because one can adapt the equations developed in Appendix B with only minor modifications.

As before, the Gaussian approximation gets only the first layer coefficients correctly, which are simply given by $\alpha_{nn} = 1$. To discuss the correction terms to the Gaussian approximation, it is necessary to write the product in (3.27) explicitly. Limiting this process to order β^8, which is sufficient for most practical purposes, gives for I_8

$$I_8 = \int_0^\infty d\beta \sin\beta P_L(\beta) \exp[-\bar{a}N\beta^2/4]\Big\{1+\sum_{i=1}^{n}\Big[c_{i4}\beta^4+c_{i6}\beta^6+\Big(c_{i8}+\sum_{j>i}^{n} c_{i4}c_{j4}\Big)\beta^8\Big]\Big\}. \tag{3.29}$$

Replacing the sums over i by some average coefficients, it is seen that Eq. (3.29) has the same β dependence as in Eq. (B.4). Therefore, one can calculate the corrections to the Gaussian approximation from Eq. (B.8) by replacing c_k with appropriate averages of c_{ik} as indicated in (3.29). Using the terminology of the last section, the second layer coefficients follow from Eq. (B.9) as

$$\{\alpha_{nn-1}\}_8 = \{\alpha_{nn-1}\}_0 - \frac{n^2(n+1)}{12\bar{a}}(3\bar{a}_1 - 2\bar{a} - 6\bar{a^2})\{\alpha_{n-1n-1}\}_0. \tag{3.30}$$

where the coefficients $\{\alpha_{nm}\}_0$ are still given by Eq. (B.3), and the bar on any quantity denotes an average as in (3.28), including the powers of a which are defined by

$$\bar{a^k}N = \sum_{i=1}^{n} a_i^k N_i. \tag{3.31}$$

Since in general $\bar{a^2} \neq \bar{a}^2$, the division of this term by $\bar{a}$, implied in Eq. (3.30), cannot be done. Thus the second layer coefficients α_{nn-1} follow from the expressions in Eq. (2.28) by simply putting a bar over all a, and replacing the middle terms by $a \to \bar{a^2}/\bar{a}$.

The situation for the third layer coefficients is slightly more complicated because there is an extra term in (3.29) involving a double sum, and c_8 is quadratic in N, which seems to require another average for a weighted with N_i^2. In fact, there is cancellation between the two terms and the third layer results look very much the same as in Eq. (B.10). To show this, consider the identity

$$\sum_{j>i} c_{i4}c_{j4} = \frac{1}{2}\Big[\Big(\sum_i c_{i4}\Big)^2 - \sum_i c_{i4}^2\Big], \tag{3.32}$$

to the coefficient of β^8 in (3.29), and substitute the values of c_{ik} from (B.6)

$$\sum_i c_{i8} + \sum_{j>i} c_{i4}c_{j4} = \frac{70}{2^7 8!}\sum_i N_i^2\left(3a_{i1} - 2a_i - 6a_i^2\right)^2$$

$$+\frac{1}{2(2^3 4!)^2}\left[\left(\sum_{i=1}^{n} N_i\left(3a_{i1}-2a_i-6a_i^2\right)\right)^2-\sum_i N_i^2\left(3a_{i1}-2a_i-6a_i^2\right)^2\right]. \tag{3.33}$$

The first and the last terms on the right hand side of Eq. (3.33) cancel each other, and the middle term requires only the averages introduced above. Thus, in complete analogy to Eq. (B.10), the third layer coefficients are given by

$$\begin{aligned}\{\alpha_{nn-2}\}_8 = \{\alpha_{nn-2}\}_0 &- \frac{n^2(n+1)}{12\bar{a}}(3\bar{a}_1-2\bar{a}-6\bar{a^2})\{\alpha_{n-1n-2}\}_0 \\ &+\frac{(n-1)^2n^2(n+1)}{180\bar{a}}\Big\{\left[-5\bar{a}_2+10\bar{a}_1-8\bar{a}+45\overline{aa}_1-30\bar{a^2}-60\bar{a^3}\right] \\ &+\frac{5(n+2)}{8\bar{a}}\left(3\bar{a}_1-2\bar{a}-6\bar{a^2}\right)^2\Big\}\{\alpha_{n-2n-2}\}_0.\end{aligned} \tag{3.34}$$

Here the average of the product is defined in the same spirit of Eq. (3.31), that is

$$\overline{aa}_1 N = \sum_{i=1}^{n} a_i a_{i1} N_i. \tag{3.35}$$

The relationship between the single- and multi-boson third layer coefficients are not as simple as in the case of the second layer, and they need to be given explicitly.

To recapitulate, the norm integral for multi-boson systems (3.26) is given by the $1/N$ expansion

$$\mathcal{N}_g(N_1,N_2,\ldots,N_n,L) = (1+\delta)\frac{2L+1}{\bar{a}N}\sum_{n=0}\frac{(-1)^n}{n!(\bar{a}N)^n}\sum_{m=0}^{n}\alpha_{nm}\bar{L}^m, \tag{3.36}$$

where $\bar{a}N$ is defined in (3.28), and the coefficients α_{nm} are given to the third layer by

$\alpha_{nn} = 1,$

$\alpha_{10} = 1+\bar{a^2}/\bar{a}-\bar{a}_1/2\bar{a},$
$\alpha_{21} = 4+6\bar{a^2}/\bar{a}-3\bar{a}_1/\bar{a},$
$\alpha_{32} = 10+18\bar{a^2}/\bar{a}-9\bar{a}_1/\bar{a},$
$\alpha_{43} = 20+40\bar{a^2}/\bar{a}-20\bar{a}_1/\bar{a},$
$\alpha_{54} = 35+75\bar{a^2}/\bar{a}-75\bar{a}_1/2\bar{a},$
$\alpha_{65} = 56+126\bar{a^2}/\bar{a}-63\bar{a}_1/\bar{a},$

$\alpha_{20} = 2+(6\bar{a^2}-4\bar{a^3}-10\bar{a}_1/3+3\overline{aa}_1-\bar{a}_2/3)/\bar{a}+6(\bar{a^2}-\bar{a}_1/2)^2/\bar{a}^2,$
$\alpha_{31} = 18+12(6\bar{a^2}-4\bar{a^3}-10\bar{a}_1/3+3\overline{aa}_1-\bar{a}_2/3)/\bar{a}+90(\bar{a^2}-\bar{a}_1/2)^2/\bar{a}^2,$

$$\alpha_{42} = 88 + 60(20\bar{a^2}/3 - 4\bar{a^3} - 11\bar{a}_1/3 + 3\overline{aa}_1 - \bar{a}_2/3)/\bar{a} + 540(\bar{a^2} - \bar{a}_1/2)^2/\bar{a}^2,$$
$$\alpha_{53} = 308 + 200(15\bar{a^2}/2 - 4\bar{a^3} - 49\bar{a}_1/12 + 3\overline{aa}_1 - \bar{a}_2/3)/\bar{a} + 2100(\bar{a^2} - \bar{a}_1/2)^2/\bar{a}^2,$$
$$\alpha_{64} = 868 + 525(42\bar{a^2}/5 - 4\bar{a^3} - 68\bar{a}_1/15 + 3\overline{aa}_1 - \bar{a}_2/3)/\bar{a} + 6300(\bar{a^2} - \bar{a}_1/2)^2/\bar{a}^2. \tag{3.37}$$

Here the various averages denoted by bars are defined in Eqs. (3.28), (3.31) and (3.35). Lifting the bars from the expressions in Eq. (3.37) one obtains the single-coherent state results in agreement with Eq. (2.28). The vibron model results are obtained from the above coefficients by substituting $a_n = 2^n a$.

3.3 Ground Band

Now consider the expectation value of the Hamiltonian (1.29-1.31) in the ground state. The final results given are accurate to the second layer, but may readily be extended by increasing the accuracy of the normalization integral used in the calculations. As in the case of the normalization integral (Section 3.2) the layer structure used in the diatomic case may be essentially retained. The sole difference is that the layers are defined by combining the powers of N_1,N_2, and N.

Operators containing only one type of boson have a simple parallel with the equivalent operators in the diatomic ground state. These results are therefore presented first. Only the type-1 boson operators will be considered here, as the type-2 results may be easily obtained from them by swapping the indices. Note that in this, and subsequent sections of the chapter, the shorthand $N = \bar{a}N$ has been adopted.

The expectation value of the one-body operator $\hat{n}_{l1}$ is given by

$$\langle \hat{n}_{l1} \rangle_L = \langle N_1, N_2, r_1, r_2 | \hat{n}_{l1} P^L_{00} | N_1, N_2, r_1, r_2 \rangle / \mathcal{N}(N_1, N_2, L), \tag{3.38}$$

where $\mathcal{N}(N_1, N_2, L)$ is the normalization. The calculation proceeds in the same way as that presented for the diatomic calculation of $\langle \hat{n}_l \rangle_L$. Thus,

$$\begin{aligned} \langle \hat{n}_{l1} \rangle_L &= \frac{1}{2N_1!N_2!F(N_1,N_2,L)} \int d\beta \sin\beta d^L_{00}(\beta) \\ &\quad \times \langle 0 | b_2^{N_1} b_2^{N_2} \hat{n}_{l1} (b^\dagger_{1R})^{N_1} (b^\dagger_{2R})^{N_2} | 0 \rangle, \end{aligned} \tag{3.39}$$

where the intrinsic matrix element is

$$\begin{aligned} &\langle 0 | b_1^{N_1} b_2^{N_1} \hat{n}_{l1} (b^\dagger_{1R})^{N_1} (b^\dagger_{2R})^{N_2} | 0 \rangle \\ &\qquad = N_1!N_2!N_1 \left(\frac{\partial b^\dagger_{1R}}{\partial b^\dagger_1} \right)^{N_1-1} \left(\frac{\partial b^\dagger_{2R}}{\partial b^\dagger_2} \right)^{N_2} \langle 0 | \frac{\partial}{\partial b^\dagger_1} \frac{\partial}{\partial b_{1R}} \hat{n}_{l1} | 0 \rangle, \\ &\qquad = N_1!N_2!N_1 [Z_1(\beta)]^{N_1-1} [Z_2(\beta)]^{N_2} x^2_{l1} d^l_{00}(\beta). \end{aligned} \tag{3.40}$$

This result demonstrates a common feature of all ground state matrix elements involving operators comprised solely of one type of boson. That is, the result (at this stage of the calculation) is the same as that of the equivalent operator in the diatomic case with the addition of a factor of $N_2![Z_2(\beta)]^{N_2}$. Thus for the operators $\hat{n}_{p1}, \hat{n}_{p1}^2, \hat{D}_1 \cdot \hat{D}_1$, we may take the equivalent diatomic calculation, add the appropriate subscript, and replace $F(N-n,L)$ by $F(N_1-n,N_2,L)$. For the one-body operator, the triatomic $\langle \hat{n}_l \rangle_L$ becomes

$$\langle \hat{n}_{l\,1} \rangle_L = \frac{N_1 x_{l1}^2}{F(N_1,N_2,L)} \sum_J \langle L0l0|J0\rangle^2 F(N_{1-1},N_2,J). \tag{3.41}$$

With appropriate substitutions, evaluation by Mathematica gives the following second layer result.

$$\begin{aligned}\langle \hat{n}_{p\,1} \rangle_L &= \frac{N_1 a_1}{2}\Big\{1+\frac{1}{N}(a_1-2)+\frac{1}{N^2}(3a_1^2+2a_2^2-4a_1)+\frac{2}{N^3}\bar{a^2}N(2-a_1) \\ &\quad -\frac{\bar{L}}{N^2}\Big[(a_1-2)+\frac{2}{N}(2+3a_1-3a_1^2-2a_2^2)+\frac{6}{N}N_1(a_1^3-a_2^2(2-a_1))\Big] \\ &\quad +\frac{\bar{L}^2}{2N^4}\Big[-4-2a_1+3a_1^2+2a_2^2+\frac{1}{N}\bar{a^2}N(2-a_1)\Big]\Big\}. \end{aligned} \tag{3.42}$$

Similarly, using the diatomic calculation for $\langle \hat{n}_p^2 \rangle_L$, the expectation value for $\langle \hat{n}_{p1}^2 \rangle_L$ can be written as

$$\langle \hat{n}_{p1}^2 \rangle_L = \frac{N_1(N_1-1)a_1^2}{4F(N_1,N_2,L)} \sum_{lJ} \langle 1010|l0\rangle^2 \langle L0l0|J0\rangle^2 F(N_{1-2},N_2,J) + \langle \hat{n}_{p1} \rangle_L. \tag{3.43}$$

The final second layer form for this expectation value is

$$\begin{aligned}\langle \hat{n}_{p1}^2 \rangle_L &= \frac{a_1 N_1^2}{4}\Big\{a_1+\frac{(2-a_1)}{N_1}+\frac{2a_1(2-a_1)}{N}-\frac{2}{N_1 N}(2-3a_1+a_1^2) \\ &\quad +\frac{2a_1}{N^2}(4-8a_1+3a_1^2)+\frac{4a_1(2-a_1)\bar{a^2}N}{N^3}+\frac{\bar{L}}{N^2}\Big[2a_1(2-a_1) \\ &\quad +\frac{2}{N_1}(2-3a_1+a_1^2)-\frac{4a_1}{N}(2-7a_1+3a_1^2)-\frac{12a_1}{N^2}\bar{a^2}N(2-a_1)\Big] \\ &\quad +\frac{\bar{L}^2}{N^4}\Big[-3a_1^2(2-a_1)+\frac{4a_1}{N}\bar{a^2}N(2-a_1)\Big]\Big\} \end{aligned} \tag{3.44}$$

where $\bar{a^k}N$ is defined by Eq. (3.31). This approach is also appropriate for the interaction $\hat{D}_1 \cdot \hat{D}_1$. Modification of the diatomic result gives

$$\begin{aligned}\langle \hat{D}_1 \cdot \hat{D}_1 \rangle_L &= \frac{N_1(N_1-1)a_1(2-a_1)}{2F(N_1,N_2,L)} \sum_{l=0}^{1} \sum_J \langle L0l0|J0\rangle^2 F(N_1-2,N_2,L) + 3\langle \hat{n}_{s\,1} \rangle_L \\ &\quad +\langle \hat{n}_{p\,1} \rangle_L, \end{aligned} \tag{3.45}$$

and the final expansion is

$$\begin{aligned}\langle \hat{D}_1 \cdot \hat{D}_1 \rangle_L &= a_1 N_1^2 \Big\{ 2 - a_1 + \frac{1}{N}(-2 + 5a_1 - 2a_1^2) + \frac{1}{a_1 N_1}(3 - 3a_1 + a_1^2) \\ &\quad - \frac{2a_1}{N^2}(4 - 8a_1 + 3a_1^2) + \frac{2}{N_1 N}(2 - 3a_1 + 2a_1^2) \\ &\quad + \frac{2a_1^2 N_1}{N^3}(2 - 5a_1 + 2a_1^2) + \frac{2a_2^2 N_2^2}{N_1 N^3}(2 - 5a_1 + 4_1^2) \\ &\quad \frac{\bar{L}}{N^2}\Big[2 - 5a_1 + 2a_1^2 - \frac{2}{N_1}(2 - 3a_1 + a_1^2) + \frac{2}{N}(2 + 3a_1 - 14a_1^2 + 6a_1^3) \\ &\quad - \frac{6\bar{a^2} N}{N^2}(2 + 5a_1 - 2a_1^2) \Big] \\ &\quad + \frac{\bar{L}^2}{N^4}\Big[-2 + a_1 + 6a_1^2 - 3a_1^3 + \frac{2\bar{a^2} N}{N}(2 - 5a_1 + 2a_1^2) \Big] \Big\}. \end{aligned} \tag{3.46}$$

(3.47)

The remaining operators in the Hamiltonian involve both type-1 and -2 bosons and are therefore not susceptible to this shorthand approach. The normal ordered forms of these operators are

$$\begin{aligned} :\hat{D}_1 \cdot \hat{D}_2: &= \sum_m \Big\{ (-)^m b^\dagger_{1,00} b^\dagger_{2,00} b_{1,1m} b_{2,1-m} + b^\dagger_{1,00} b^\dagger_{2,1m} b_{1,1m} b_{2,00} \\ &\quad + b^\dagger_{1,1m} b^\dagger_{2,00} b_{1,00} b_{2,1m} + (-)^m b^\dagger_{1,1-m} b^\dagger_{2,1m} b_{1,00} b_{2,00} \Big\}, \end{aligned} \tag{3.48}$$

$$:\hat{n}_{1p} \cdot \hat{n}_{2p}: = \sum_{mn} b^\dagger_{1,1m} b^\dagger_{2,1n} b_{1,1m} b_{2,1n}, \tag{3.49}$$

$$\begin{aligned} :\hat{M}'_4: &= \sum_m \Big\{ b^\dagger_{1,00} b^\dagger_{2,1m} b_{1,00} b_{2,1m} - b^\dagger_{1,00} b^\dagger_{2,1m} b_{1,1m} b_{2,00} \\ &\quad - b^\dagger_{1,1m} b^\dagger_{2,00} b_{1,00} b_{2,1m} + b^\dagger_{1,1m} b^\dagger_{2,00} b_{1,1m} b_{2,00} \Big\}, \end{aligned} \tag{3.50}$$

$$:\hat{M}_3: = \sum_m \Big\{ b^\dagger_{1,10} b^\dagger_{2,1m} b_{1,10} b_{2,1m} - b^\dagger_{1,10} b^\dagger_{2,1m} b_{1,1m} b_{2,10} \Big\} \tag{3.51}$$

The expectation value of M_3 vanishes in the ground band of linear molecules (and in the stretching bands). Since it plays a relatively minor role in symmetry breaking, it will not be discussed further. For the same reason, the M_3 part has been excluded from M_4 by introducing $M'_4 = M_4 - M_3$. The corresponding expectation values are given by

$$\begin{aligned} \langle :\hat{D}_1 \cdot \hat{D}_2: \rangle_L &= \frac{2N_1 N_2}{F(N_1, N_2, L)} x_{1,0} x_{1,1} x_{2,0} x_{2,1} \sum_{J=0}^{1} \sum_l (\delta_{l0} + \delta_{l1}) \langle L0l0 | J0 \rangle^2, \\ &\quad \times F(N_1 - 1, N_2 - 1, J) \end{aligned} \tag{3.52}$$

$$\langle :\hat{n}_{1p} \cdot \hat{n}_{2p}: \rangle_L = \frac{N_1 N_2}{3F(N_1, N_2, L)} x_{1,1}^2 x_{2,1}^2 \sum_{J=0}^{2} \sum_l (\delta_{l0} + 2\delta_{l2}) \langle L0l0 | J0 \rangle^2,$$

$$\times F(N_1-1,N_2-1,J) \tag{3.53}$$

$$\langle :M_4': \rangle_L = \frac{N_1N_2}{F(N_1,N_2,L)}(-x_{1,1}x_{2,0}+x_{1,0}x_{2,0})^2\sum_{J=0}^{1}\langle L010|J0\rangle^2 \times F(N_1-1,N_2-1,J). \tag{3.54}$$

Finally, carrying the necessary algebra, the following second layer expressions are obtained

$$\begin{aligned}\langle \hat{D}_1\cdot\hat{D}_2\rangle_L &= \frac{(2-a_1)(2-a_2)}{4}r_1r_2N_1N_2\Big\{1-\frac{1-a_1-a_2}{N} \\ &\quad -\frac{2}{N^2}(a_1-a_1^2+a_2-a_2^2-a_1a_2)+\frac{2\bar{a^2}N}{N^3}(1-a_1-a_2) \\ &\quad +\frac{\bar{L}}{N^2}\Big[1-a_1-a_2-\frac{6\bar{a^2}N}{N^2}(1-a_1-a_2) \\ &\quad +\frac{1}{N}(1+a_1-2a_1^2+a_2-2a_2^2-2a_1a_2)\Big] \\ &\quad +\frac{\bar{L}^2}{N^4}\Big[-1+a_1^2+a_2^2+a_1a_2+\frac{2}{N}\bar{a^2}N(1-a_1-a_2)\Big]\Big\},\end{aligned} \tag{3.55}$$

$$\begin{aligned}\langle \hat{n}_{p1}\cdot\hat{n}_{p2}\rangle_L &= \frac{a_1a_2N_1N_2}{4}\Big\{1-\frac{4+a_1+a_2}{N} \\ &\quad +\frac{2}{N^2}(4-4a_1+a_1^2-4a_2+a_2^2+a_1a_2)+\frac{2}{N^3}\bar{a^2}N(4-a_1-a_2) \\ &\quad +\frac{\bar{L}}{N^2}\Big[4-a_1-a_2-\frac{2}{N}(4-7a_1+2a_1^2-7a_2+2a_2^2+2a_1a_2) \\ &\quad -\frac{6}{N^2}\bar{a^2}N(4-a_1-a_2)\Big] \\ &\quad +\frac{\bar{L}^2}{N^4}\Big[-3a_1+a_1^2-3a_2+a_2^2+a_1a_2+\frac{2}{N}\bar{a^2}N(4-a_1-a_2)\Big]\Big\}.\end{aligned} \tag{3.56}$$

$$\begin{aligned}\langle M_4'\rangle_L &= \frac{N_1N_2}{2}(a_1+a_2-a_1a_2+(2-a_1)(2-a_2)r_1r_2) \\ &\quad \times\Big\{1-\frac{2-a_1-a_2}{N}-\frac{2}{N^2}(2a_1-a_1^2+2a_2-a_2^2-a_1a_2)+\frac{2}{N^3}\bar{a^2}N(2-a_1-a_2) \\ &\quad +\frac{\bar{L}}{N^2}\Big[2-a_1-a_2+\frac{2}{N}(2+3a_1-2a_1^2+3a_2-2a_2^2-2a_1a_2) \\ &\quad -\frac{6}{N^2}\bar{a^2}N(2-a_1-a_2)\Big] \\ &\quad -\frac{\bar{L}^2}{N^4}\Big[2+a_1+a_1^2+a_2-a_2^2-a_1a_2)+\frac{2}{N}\bar{a^2}N(2-a_1-a_2)\Big]\Big\}.\end{aligned} \tag{3.57}$$

Combining all the individual expectation values derived above leads a rather long expression for the ground-band energy, which is not repeated. The associated

variational problem would require solution of the mean fields to order $1/N$ for the second layer energy. (Recall that a given layer in mean fields contributes only to the next and higher layers in energies.) To the leading order, the projected ground energy is the same as the mean field theory result (3.7), whose variation has already been discussed. These leading order solutions for the mean fields are sufficient for the purposes of systematic investigations of symmetry breaking effects. Therefore, the $1/N$ corrections to the mean fields, which lead to very lengthy expressions, are not presented here.

3.4 Vibrational Bands

There are three first vibrational overtones for a triatomic molecule. These correspond to a symmetric and antisymmetric stretching modes and an (antisymmetric) bending mode (the spurious symmetric bending state represents the rotation of the molecule as a whole). Following [5], which develops the $1/N$ formalism for the neutron-proton degree of freedom in the IBM, these excited states are defined as

symmetric stretching:

$$|\phi_0\rangle = \frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}(b_1^\dagger)^{N_1-1}b_1'^\dagger(b_2^\dagger)^{N_2}|0\rangle + \frac{\sin\gamma}{[N_1!(N_1-1)!]^{1/2}}(b_1^\dagger)^{N_1}(b_2^\dagger)^{N_2-1}b_2'^\dagger|0\rangle, \tag{3.58}$$

antisymmetric stretching:

$$|\phi_{0_M}\rangle = \frac{\sin\gamma}{[(N_1-1)!N_2!]^{1/2}}(b_1^\dagger)^{N_1-1}b_1'^\dagger(b_2^\dagger)^{N_2}|0\rangle - \frac{\cos\gamma}{[N_1!(N_1-1)!]^{1/2}}(b_1^\dagger)^{N_1}(b_2^\dagger)^{N_2-1}b_2'^\dagger|0\rangle, \tag{3.59}$$

symmetric bending:

$$|\phi_1\rangle = \frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}(b_1^\dagger)^{N_1-1}b_1''^\dagger(b_2^\dagger)^{N_2}|0\rangle + \frac{\sin\gamma}{[N_1!(N_1-1)!]^{1/2}}(b_1^\dagger)^{N_1}(b_2^\dagger)^{N_2-1}b_2''^\dagger|0\rangle, \tag{3.60}$$

antisymmetric bending:

$$|\phi_{1_M}\rangle = \frac{\sin\gamma}{[(N_1-1)!N_2!]^{1/2}}(b_1^\dagger)^{N_1-1}b_1''^\dagger(b_2^\dagger)^{N_2}|0\rangle - \frac{\cos\gamma}{[N_1!(N_1-1)!]^{1/2}}(b_1^\dagger)^{N_1}(b_2^\dagger)^{N_2-1}b_2''^\dagger|0\rangle. \tag{3.61}$$

γ is a further variational parameter, or 'mixing angle'. When considering the bending states, γ is determined by ensuring that the normalization of the symmetric state vanishes. This eliminates the spurious state. For the stretching states, γ is

determined by the usual variational procedure. Note that K in $|\phi_K\rangle$ denotes the quantum number for projection to the body-fixed axis. The boson operators b'_i, b''_i are defined as

$$\begin{aligned} b'_i &= [1+r_i^2]^{-1/2}(r_i s_i - p_{i,0}), \\ b''_i &= p_{i,1}. \end{aligned} \tag{3.62}$$

3.4.1 Symmetric Stretching

The normalization for this state is given by

$$\begin{aligned} \mathcal{N}_S(N_1,N_2,L) &= \frac{2L+1}{2}\int_0^\pi d\beta \sin\beta P_L(\cos\beta) \\ &\times\left(\frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}\langle 0|b_1^{N_1-1}b'_1 b_2^{N_2} + \frac{\sin\gamma}{[N_1!(N_1-1)!]^{1/2}}\langle 0|b_1^{N_1}b_2^{N_2-1}b'_2\right) \\ &\times\left(\frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}(b^\dagger_{1R})^{N_1-1}b'^\dagger_{1R}(b^\dagger_{2R})^{N_2}|0\rangle\right. \\ &\left.+\frac{\sin\gamma}{[N_1!(N_1-1)!]^{1/2}}(b^\dagger_{1R})^{N_1}(b^\dagger_{2R})^{N_2-1}b'^\dagger_{2R}|0\rangle\right). \end{aligned} \tag{3.63}$$

Expanding, the intrinsic matrix element gives

$$\begin{aligned} &\cos^2\gamma\left[Z'_1[\beta]Z_1^{N_1-1}[\beta] + (N_1-1)Y_1^2[\beta]Z_1^{N_1-2}[\beta]\right]Z_2^{N_2}[\beta] \\ &+2\cos\gamma\sin\gamma\sqrt{N_1N_2}Y_1[\beta]Y_2[\beta]Z_1^{N_1-1}[\beta]Z_2^{N_2-1}[\beta] \\ &+\sin^2\gamma Z_1^{N_1}[\beta]\left[Z'_b[\beta]Z_2^{N_2-1}[\beta] + (N_2-1)Y_2^2[\beta]\right], \end{aligned} \tag{3.64}$$

where, Y_i and Z'_i are obtained from the Z and Y used in the diatomic calculation by the addition of appropriate subscripts. Upon expansion, the second layer symmetric stretching normalization to order $1/N^4$ is given by

$$\begin{aligned} \mathcal{N}_S(N_1,N_2,L) &= 1+\frac{1}{N}\Big(-2+a_1+a_2+(a_1-a_2)\cos(2\gamma)+n_s\Big) \\ &-\frac{\bar{L}}{N}\Big[1-\frac{1}{N}\Big(3+2a_1+2a_2+2(a_1-a_2)\cos(2\gamma)+3n_s\Big)\Big] \\ &+\frac{\bar{L}^2}{2N^2}\Big[1+\frac{1}{3N}\Big(10-9a_1-9a_2-9(a_1-a_2)\cos(2\gamma)+3n_s\Big)\Big] \\ &-\frac{\bar{L}^3}{6N^3}\Big[1-\frac{1}{N}\Big(3-4a_1-4a_2-4(a_1-a_2)\cos(2\gamma)\Big)\Big] \\ &+\frac{\bar{L}^4}{24N^4}, \end{aligned} \tag{3.65}$$

where,

$$\begin{aligned} n_s &= \frac{1}{N}\Big[\sum_{i=1}^{2}N_i a_i\,(2-2a_i+(2-a_i)\cos(2\gamma)) \\ &\qquad +(N_1N_2)^{1/2}2(2-a_1)(2-a_2)r_1r_2\sin(2\gamma)\Big]. \end{aligned} \tag{3.66}$$

The expectation values of one- and two-body terms in the Hamiltonian are presented below. Note that the results obtained for these states are extremely lengthy. For this reason, although the expansions have been calculated to second layer, only the first layer results are presented in the following sections. The second layer results are given in Appendix F. An intermediate step is also presented for each operator which in principle allows the calculation to be extended to any order.

The expectation values of the one-body operators in the symmetric state are given by

$$\begin{aligned}
\langle \hat{n}_{pi} \rangle_{1L} &= \frac{1}{2F_1(N_1,N_2,L)} \int d\beta \sin\beta d^L_{00}(\beta) \\
&\times \left(\frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}} \langle 0| b_1^{N_1-1} b'_1 b_2^{N_2} + \frac{\sin\gamma}{[N_1!(N_2-1)!]^{1/2}} \langle 0| b_1^{N_1} b_2^{N_2-1} b'_2 \right) \hat{n}_{pi} \\
&\times \left(\frac{\cos\gamma}{[(N_1-1)!N_b!]^{1/2}} |0\rangle (b^\dagger_{1R})^{N_1-1} b'^\dagger_{1R} (b^\dagger_{2R})^{N_2} \right. \\
&\left. + \frac{\sin\gamma}{[N_1!(N_2-1)!]^{1/2}} |0\rangle (b^\dagger_{1R})^{N_1} (b^\dagger_{2R})^{N_2-1} b'^\dagger_{2R} \right).
\end{aligned} \tag{3.67}$$

The intrinsic matrix element for $i = 1$ can be expanded as

$$\begin{aligned}
&\cos^2\gamma \left[\left(\frac{\partial}{\partial b'^\dagger_1} \frac{\partial}{\partial b'_{1R}} \hat{n}_{p1} \right) Z_1^{N_1-1}[\beta] + (N_1-1) \left(\frac{\partial}{\partial b'^\dagger_1} \frac{\partial}{\partial b_{1R}} \hat{n}_{p1} \right) Y_1[\beta] Z_1^{N_1-2}[\beta] \right. \\
&+ (N_1-1) \left(\frac{\partial}{\partial b^\dagger_1} \frac{\partial}{\partial b'_{1R}} \hat{n}_{p1} \right) Y_1[\beta] Z_1^{N_1-2}[\beta] \\
&+ (N_1-1) \left(\frac{\partial}{\partial b^\dagger_1} \frac{\partial}{\partial b_{1R}} \hat{n}_{p1} \right) Z'_1[\beta] Z_1^{N_1-2}[\beta] \\
&\left. + \frac{(N_1-1)(N_1-2)}{2} \left(\frac{\partial}{\partial b^\dagger_1} \frac{\partial}{\partial b_{1R}} \hat{n}_{p1} \right) Y_1^2[\beta] Z_1^{N_1-3}[\beta] \right] Z_2^{N_2}[\beta] \Big] \\
&+ \cos\gamma \sin\gamma \sqrt{N_1 N_2} \left[\left(\frac{\partial}{\partial b'^\dagger_1} \frac{\partial}{\partial b_{1R}} \hat{n}_{p1} \right) Z_1^{N_1-1}[\beta] + \left(\frac{\partial}{\partial b^\dagger_1} \frac{\partial}{\partial b'_{1R}} \hat{n}_{p1} \right) Z_1^{N_1-1}[\beta] \right. \\
&\left. + 2(N_1-1) \left(\frac{\partial}{\partial b^\dagger_1} \frac{\partial}{\partial b_{1R}} \hat{n}_{p1} \right) Y_1[\beta] Z_1^{N_1-2}[\beta] \right] Y_2[\beta] Z_2^{N_2-1}[\beta] \Big] \\
&+ \sin^2\gamma N_1 Z_1^{N_1-1} \left(\frac{\partial}{\partial b^\dagger_1} \frac{\partial}{\partial b_{1R}} \hat{n}_{p1} \right) \Big[Z'_2[\beta] Z_2^{N_2-1}[\beta] + (N_2-1) Y_2^2[\beta] Z_2^{N_2-2}[\beta] \Big].
\end{aligned} \tag{3.68}$$

Substituting this result in the matrix element and using the normalization integral, one obtains the following intermediate result

$$\langle \hat{n}_{p1} \rangle_L = \sum_I \sum_{J=0}^{3} \langle L0J0|I0\rangle^2 \Big\{ \cos^2\gamma \frac{1}{2} \Big[(2-a_1)\delta_{J1} F(N_1-1, N_2, I)$$

$$
\begin{aligned}
&+\frac{1}{2}(N_1{-}1)a_1((2-a_1)(\delta_{J0}+2\delta_{J2})-(4-3a_1)\delta_{J1})F(N_1{-}2,N_2,I)\\
&-\frac{1}{30}(N_1{-}1)(N_1{-}2)(2-a_1)a_1^2(5(\delta_{J0}{+}2\delta_{J2})-3(4\delta_{J1}{+}\delta_{J3}))F(N_1{-}3,N_2,I)\Big]\\
&+\cos\gamma\sin\gamma\sqrt{N_1N_2}\frac{1}{6}(2-a_1)(2-a_2)r_1r_2\Big[(\delta_{J0}-3\delta_{J1}+2\delta_{J2})F(N_1{-}1,N_2{-}1,I)\\
&-\frac{1}{5}(N_1{-}1)a_1(5(\delta_{J0}+2\delta_{J2})-3(4\delta_{J1}+\delta_{J3}))F(N_1{-}2,N_2{-}1,I)\Big]\\
&+\sin^2\gamma N_1a_1\frac{1}{12}\Big[((2-a_2)(\delta_{J0}+2\delta_{J2})+3a_2\delta_{J1})F(N_1{-},N_2{-}1,I)\\
&+\frac{1}{5}(N_2{-}1)(2-a_2)a_2(5(\delta_{J0}+2\delta_{J2})\\
&-3(\delta_{J1}+\delta_{J3}))F(N_1{-}1,N_2{-}2,I)\Big]\Big\}. \qquad (3.69)
\end{aligned}
$$

This expression can be evaluated to an arbitrary accuracy using Mathematica. Below, $\langle\hat{n}_{p1}\rangle_L$ is given to the first layer. Second layer contribution is given in Appendix F

$$
\begin{aligned}
\langle\hat{n}_{p1}\rangle_L &= \frac{N_1a_1}{2}+(1-a_1)\cos^2(\gamma)-\frac{N_1}{2N}(2-a_1)a_1(2+\cos(2\gamma))\\
&-\frac{(N_1N_2)^{1/2}}{2N}(2-a_1)(2-a_2)r_1r_2\\
&+\frac{\bar{L}}{2N^2}\left[N_1(2-a_1)a_1(2+\cos(2\gamma))+(N_1N_2)^{1/2}(2-a_1)(2-a_2)r_1r_2\sin(2\gamma)\right]. \qquad (3.70)
\end{aligned}
$$

For the two-body operators comprised of only one type of bosons, for example $\hat{O}_{11}$, the matrix element required for the expectation value in the symmetric state is given by

$$
\begin{aligned}
&\left(\frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}\langle 0|b_1^{N_1-1}b_1'b_2^{N_2}+\frac{\sin\gamma}{[N_1!(N_2-1)!]^{1/2}}\langle 0|b_1^{N_1}b_2^{N_2-1}b_2'\right)\hat{O}_{11}\\
&\times\Big(\frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}\langle 0|(b_{1R}^\dagger)^{N_1-1}b_{1R}'^\dagger(b_{2R}^\dagger)^{N_2}\\
&\quad+\frac{\sin\gamma}{[N_1!(N_2-1)!]^{1/2}}\langle 0|(b_{1R}^\dagger)^{N_1}(b_{2R}^\dagger)^{N_2-1}b_{2R}'^\dagger\Big)\\
=\;&\cos^2\gamma\Big[\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_{1R}'}\hat{O}_{11}\right)Z_1^{N_1-1}[\beta]+(N_1-1)\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]\\
&+(N_1-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}'}\hat{O}_{11}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]\\
&+(N_1-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1'[\beta]Z_1^{N_1-2}[\beta]\\
&+(N_1-1)\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}'}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1^{N_1-2}[\beta]
\end{aligned}
$$

$$
\begin{aligned}
&+(N_1-1)(N_1-2)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Y_1^2[\beta]Z_1^{N_1-2}[\beta]\\
&+\frac{(N_1-1)(N_1-2)}{2}\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b'_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Y_1[\beta]Z_1^{N_1-3}[\beta]\\
&+\frac{(N_1-1)(N_1-2)}{2}\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Y_1[\beta]Z_1^{N_1-3}[\beta]\\
&+\frac{(N_1-1)(N_1-2)}{4}\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1'[\beta]Z_1^{N_1-3}[\beta]\\
&+\frac{(N_1-1)(N_1-2)(N_1-3)}{4}\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Y_1^2[\beta]Z_1^{N_1-4}[\beta]\Big]Z_2^{N_2}[\beta]\\
+\;&\cos\gamma\sin\gamma\sqrt{N_1N_2}\Big[\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1^{N_1-1}[\beta]+\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b'_{1R}}\hat{O}_{11}\right)Z_1^{N_1-1}[\beta]\\
&+2(N_1-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]\\
&+\frac{(N_1-1)}{2}\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1^{N_1-2}[\beta]\\
&+\frac{(N_1-1)}{2}\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b'_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1^{N_1-2}[\beta]\\
&+\frac{(N_1-1)(N_1-2)}{2}\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Y_1[\beta]Z_1^{N_1-3}[\beta]\Big]Y_2[\beta]Z_2^{N_2-1}[\beta]\\
+\;&\sin^2\gamma\Big[N_1\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1^{N_1-1}[\beta]\\
&+\frac{N_1(N_1-1)}{4}\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{1R}}\hat{O}_{11}\right)Z_1^{N_1-2}[\beta]\Big]\\
&\times\Big[Z_2'[\beta]Z_2^{N_2-1}[\beta]+(N_2-1)Y_2^2[\beta]Z_2^{N_2-2}[\beta]\Big].
\end{aligned}
\tag{3.71}
$$

The equivalent result for $\hat{O}_{22}$ is simply obtained by swapping the indices 1,2, and by exchanging $\sin\gamma$ and $\cos\gamma$. Similarly, the remaining two-body operators that are comprised of both types of bosons, $\hat{O}_{12}$, have the expectation value

$$
\begin{aligned}
&\left(\frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}\langle 0|b_1^{N_1-1}b_1'b_2^{N_2}+\frac{\sin\gamma}{[N_1!(N_2-1)!]^{1/2}}\langle 0|b_1^{N_1}b_2^{N_2-1}b_2'\right)\hat{O}_{12}\\
&\times\Big(\frac{\cos\gamma}{[(N_1-1)!N_2!]^{1/2}}\langle 0|(b_{1R}^\dagger)^{N_1-1}b_{1R}'^\dagger(b_{2R}^\dagger)^{N_2}\\
&+\frac{\sin\gamma}{[N_1!(N_2-1)!]^{1/2}}\langle 0|(b_{1R}^\dagger)^{N_1}(b_{2R}^\dagger)^{N_2-1}b_{2R}'^\dagger\Big)\\
=\;&\cos^2\gamma\Big[\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Z_1^{N_1-1}[\beta]\\
&+(N_1-1)\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{2R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]
\end{aligned}
$$

$$
\begin{aligned}
&+(N_1-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]\\
&+(N_1-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Z'_1[\beta]Z_1^{N_1-2}[\beta]\\
&+(N_1-1)(N_1-2)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Y_2^2[\beta]Z_1^{N_1-3}[\beta]\Big]N_2Z_2^{N_2-1}[\beta]\\
+\;&\cos\gamma\sin\gamma\sqrt{N_1N_2}\Big[\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b'_{2R}}\hat{O}_{12}\right)Z_1^{N_1-1}[\beta]Z_2^{N_2-1}[\beta]\\
&+\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Z_1^{N_1-1}[\beta]Z_2^{N_2-1}[\beta]\\
&+(N_1-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{2R}}\frac{\partial}{\partial b'_{2R}}\hat{O}_{12}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]Z_2^{N_2-1}[\beta]\\
&+(N_1-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]Z_2^{N_2-1}[\beta]\\
&+(N_2-1)\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Z_1^{N_1-1}[\beta]Y_1[\beta]Z_2^{N_2-2}[\beta]\\
&+(N_2-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Z_1^{N_1-1}[\beta]Y_1[\beta]Z_2^{N_2-2}[\beta]\\
&+2(N_1-1)(N_2-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Y_1[\beta]Z_1^{N_1-2}[\beta]Y_2[\beta]Z_2^{N_2-2}[\beta]\Big]\\
+\;&\sin^2\gamma N_1Z_1^{N_1-1}[\beta]\Big[\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b'_{2R}}\hat{O}_{12}\right)Z_2^{N_2-1}[\beta]\\
&+(N_2-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Y_2[\beta]Z_2^{N_2-2}[\beta]\\
&+(N_2-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b'_{2R}}\hat{O}_{12}\right)Y_2[\beta]Z_2^{N_2-2}[\beta]\\
&+(N_2-1)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Z'_2[\beta]Z_2^{N_2-2}[\beta]\\
&+(N_2-1)(N_2-2)\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1R}}\frac{\partial}{\partial b_{2R}}\hat{O}_{12}\right)Y_2^2[\beta]Z_2^{N_2-3}[\beta]\Big]. \qquad (3.72)
\end{aligned}
$$

Using the operator derivatives given in Appendix E in the above expressions, the expectation values of the two-body interactions in the Hamiltonian can be evaluated in a straightforward manner. As before, only one intermediate step before substituting the normalization integral is given. These can be used to generate higher order terms. The final results are given to the first layer and the second layers are relegated to Appendix F

$$
\langle\hat{n}_{p1}^2\rangle_L = \sum_I\sum_{J=0}^{4}\langle L0J0|I0\rangle^2\Big\{\cos^2\gamma\Big[\frac{2-a_1}{2}\delta_{J1}F(N_1{-}1,N_2,I)
$$

$$
\begin{aligned}
&+\frac{a_1}{12}(N_1{-}11)\,(7(2-a_1)(\delta_{J0}+2\delta_{J2})+3(3a_1-4)\delta_{J1})\,F(N_1{-}12,N_2,I)\\
&+(N_1{-}11)(N_1{-}2)\frac{a_1^2}{120}\,(5(2-a_1)(\delta_{J0}+2\delta_{J2})+3(7a_1-12)(23\delta_{J1}+12\delta_{J3}))\\
&\qquad\times F(N_1{-}3,N_2,I)\\
&+(N_1{-}1)(N_1{-}2)(N_1{-}3)\frac{a_1^3(2-a_1)}{840}\,(28\delta_{J0}-63\delta_{J1}+65\delta_{J2}-42\delta_{J3}+12\delta_{J4})\\
&\qquad\times F(N_1{-}4,N_2,I)\Big]\\
&+\cos\gamma\sin\gamma\sqrt{N_1N_2}\frac{1}{6}r_1r_2(2-a_1)(2-a_2)\Big[(\delta_{J0}-3\delta_{J1}+2\delta_{J2})\\
&\qquad\times F(N_1{-}1,N_2{-}1,I)\\
&+\frac{a_1}{5}(N_1{-}1)\,(-10\delta_{J0}+21\delta_{J1}-20\delta_{J2}+9\delta_{J3})\,F(N_1{-}2,N_2{-}1,I)\\
&+\frac{a_1^2}{70}(N_1{-}1)(N_1{-}2)\,(28\delta_{J0}-63\delta_{J1}+65\delta_{J2}-42\delta_{J3}+12\delta_{J4})\\
&\qquad\times F(N_1{-}3,N_2{-}1,I)\Big]\\
&+\sin^2\gamma N_1\frac{a_1}{12}\Big[(3a_2\delta_{J1}+(2-a_2)(\delta_{J0}+2\delta_{J2}))\,F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{a_1}{10}\,(5a_2\delta_{J0}+9(2-a_2)\delta_{J1}+10a_2\delta_{J2}+6(2-a_2)\delta_{J3})\\
&\qquad\times F(N_1{-}2,N_2{-}1,I)\\
&+(N_2{-}1)\frac{a_2(2-a_2)}{10}\,(-10\delta_{J0}+24\delta_{J1}-20\delta_{J2}+6\delta_{J3})\,F(N_1{-}1,N_2{-}2,I)\\
&+(N_1{-}1)(N_2{-}1)\frac{a_1a_2(2-a_2)}{70}\,(28\delta_{J0}-63\delta_{J1}+65\delta_{J2}-42\delta_{J3}+12\delta_{J4})\\
&\qquad\times F(N_1{-}2,N_2{-}2,I)\Big]\Big\},
\end{aligned}
\tag{3.73}
$$

$$
\begin{aligned}
\langle\hat{n}_{p1}^2\rangle_L &= \frac{N_1^2a_1^2}{4}+\frac{N_1}{4}a_1(6-4a_1+(4-3a_1)\cos(2\gamma))\\
&\quad-\frac{N_1^2}{2N}(2-a_1)a_1^2(2+\cos(2\gamma))\\
&\quad-\frac{N_1^{3/2}N_2^{1/2}}{2N}(2-a_1)(2-a_2)a_1r_1r_2\sin(2\gamma)\\
&\quad-\frac{\bar{L}}{2N^2}\Big[N_1^2(2-a_1)a_1^2(2+\cos(2\gamma))\\
&\qquad+N_1^{3/2}N_2^{1/2}(2-a_1)(2-a_2)a_1r_1r_2\sin(2\gamma)\Big].
\end{aligned}
\tag{3.74}
$$

$$
\langle\hat{n}_{p1}\hat{n}_{p2}\rangle_L = \sum_I\sum_{J=0}^{4}\langle L0J0|I0\rangle^2\Big\{\cos^2\gamma N_2\frac{a_2}{12}\Big[(2-a_1)(\delta_{J0}+2\delta_{J2})
$$

$$
\begin{aligned}
&\times F(N_1{-}1, N_2{-}1, I) \\
&+(N_1{-}1, N_2{-}1)\frac{a_1}{10}\left(5(7a_1-4)\delta_{J0}+(2-a_1)(27\delta_{J1}-20\delta_{J2}+18\delta_{J3})\right) \\
&\times F(N_1{-}2, N_2{-}1, I) \\
&+(N_1{-}1)(N_1{-}2)\frac{a_1^2(2-a_1)}{70}\left(28\delta_{J0}-63\delta_{J1}+65\delta_{J2}-42\delta_{J3}+12\delta_{J4}\right) \\
&\times F(N_1{-}3, N_2{-}1, I)\Big] \\
&+\cos\gamma\sin\gamma\sqrt{N_1N_2}\frac{1}{6}r_1r_2(2-a_1)(2-a_2)\Big[(\delta_{J0}+2\delta_{J2})\,F(N_1{-}1, N_2{-}1, I) \\
&+(N_1{-}1)\frac{a_1}{10}\left(-5\delta_{J0}+9\delta_{J1}-10\delta_{J2}+6\delta_{J3}\right)F(N_1{-}2, N_2{-}1, I) \\
&+(N_2{-}1)\frac{a_2}{10}\left(-5\delta_{J0}+9\delta_{J1}-10\delta_{J2}+6\delta_{J3}\right)F(N_1{-}1, N_2{-}2, I) \\
&+(N_1{-}1)(N_2{-}1)\frac{a_1a_2}{70}\left(28\delta_{J0}-63\delta_{J1}+65\delta_{J2}-42\delta_{J3}+12\delta_{J4}\right) \\
&\times F(N_1{-}2, N_2{-}2, I)\Big] \\
&+\sin^2\gamma N_1\frac{a_1}{12}\Big[(2-a_2)(\delta_{J0}+2\delta_{J2})F(N_1{-}1, N_2{-}1, I) \\
&+(N_2{-}1)\frac{a_2}{10}\left(5(7a_2-4)\delta_{J0}+(2-a_2)(27\delta_{J1}-20\delta_{J2}+18\delta_{J3})\right) \\
&\times F(N_1{-}1, N_2{-}2, I) \\
&+(N_2{-}1)(N_2{-}2)\frac{a_2^2(2-a_2)}{70}\left(28\delta_{J0}-63\delta_{J1}+65\delta_{J2}-42\delta_{J3}+12\delta_{J4}\right) \\
&\times F(N_1{-}1, N_2{-}3, I)\Big]\Big\}, \qquad (3.75)
\end{aligned}
$$

$$
\begin{aligned}
\langle\hat{n}_{p1}\hat{n}_{p2}\rangle_L &= \frac{N_1N_2a_1a_2}{4}+\frac{1}{2}\left(N_1a_1(1-a_2)\sin^2(\gamma)+N_2a_2(1-a_1)\cos^2(\gamma)\right) \\
&+\frac{1}{2}(N_1N_2)^{1/2}(2-a_1)(2-a_2)r_1r_2\sin(2\gamma) \qquad (3.76) \\
&-\frac{1}{4N}N_1N_2a_1a_2(-8+2a_1+2a_2+(a_1-a_2)\cos(2\gamma)) \\
&+\frac{\tilde{L}}{4N}\Big[N_1^{1/2}N_2^{1/2}(2-a_1)(2-a_2)r_1r_2\sin(2\gamma) \\
&+\frac{1}{N}N_1N_2a_1a_2(8-2a_1-2a_2+(a_1-a_2)\cos(2\gamma))\Big]. \qquad (3.77)
\end{aligned}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot\hat{D}_1\rangle_L &= \sum_I\sum_{J=0}^{3}\langle L0J0|I0\rangle^2\Big\{\cos^2\gamma\frac{1}{2}\Big[(3a_1\delta_{J0}+(2-a_1)\delta_{J1})\,F(N_1{-}1, N_2, I) \\
&+(N_1{-}1)a_1\left((2-a_1)(\delta_{J0}+\delta_{J2})+2(5-11a_1+5a_1^2)\delta_{J1}\right)F(N_1{-}2, N_2, I) \\
&+(N_1{-}1)(N_1{-}2)\frac{a_1(2-a_1)}{10}(5(2+a_1)\delta_{J0}+(19a_1-20)\delta_{J1}+5(6-5a_1)\delta_{J2}
\end{aligned}
$$

$$
\begin{aligned}
&+a_1\delta_{J3})F(N_1{-}3,N_2,I)\\
&+(N_1{-}1)(N_1{-}2)(N_1{-}3)\frac{a_1^2(2-a_1)^2}{30}\,(5\delta_{J0}-3\delta_{J1}-5\delta_{J2}+3\delta_{J3})\\
&\times F(N_1{-}4,N_2,I)\Big]\\
&+\cos\gamma\sin\gamma\sqrt{N_1N_2}\frac{1}{3}(2-a_1)(2-a_2)r_1r_2\Big[(5\delta_{J0}-6\delta_{J1}+\delta_{J2})\\
&\times F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{10}\,(5(8-3a_1)\delta_{J0}+3(19a_1-30)\delta_{J1}+5(10-9a_1)\delta_{J2}+3a_1\delta_{J3})\\
&\times F(N_1{-}2,N_2{-}1,I)\\
&+(N_1{-}1)(N_1{-}2)\frac{1}{10}(2-a_1)a_1\,(5\delta_{J0}-3\delta_{J1}-5\delta_{J2}+3\delta_{J3})\\
&\times F(N_1{-}3,N_2{-}1,I)\Big]\\
&+\sin^2\gamma N_1\frac{1}{6}\Big[((a_1+9a_2-5a_1a_2)\delta_{J0}+3(6-3a_1-3a_2+2a_1a_2)\delta_{J1}\\
&+(2a_1-a_1a_2)\delta_{J2})F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)(2-a_1)a_1\,((1+a_2)\delta_{J0}+3\delta_{J1}+(2-a_2)\delta_{J2})\,F(N_1{-}2,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{10}(2-a_2)a_2(5(12-7a_1)\delta_{J0}+3(19a_1-30)\delta_{J1}+5(6-5a_1)\delta_{J2}\\
&+3a_1\delta_{J3})F(N_1{-}1,N_2{-}2,I)\\
&+(N_1{-}1)(N_2{-}1)\frac{1}{10}(2-a_1)(2-a_2)a_1a_2\,(5\delta_{J0}-3\delta_{J1}-5\delta_{J2}+3\delta_{J3})\\
&\times F(N_1{-}2,N_2{-}2,I)\Big]\Big\},
\end{aligned}
\tag{3.78}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot D_1\rangle_L \;=\;& N_1^2(2-a_1)a_1\\
&+N_1\left((1-4a_1)(4-a_1)-(1-6a_1+3a_1^2)\cos(2\gamma)\right)\\
&+\frac{N_1^2}{N}(2-a_1)a_1(-3+4a_1-2(1-a_1)\cos(2\gamma))\\
&-\frac{N_1^{3/2}N_2^{1/2}}{N}2(2-a_1)(1-a_1)(2-a_2)r_1r_2\sin(2\gamma)\\
&+\frac{\bar{L}}{N^2}\Big[N_1^2(2-a_1)a_1(3-4a_1-2(1-a_1)\cos(2\gamma))\\
&+2N_1^{3/2}N_2^{1/2}(2-a_1)(1-a_1)(2-a_2)r_1r_2\sin(2\gamma)\Big].
\end{aligned}
\tag{3.79}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot\hat{D}_2\rangle_L \;=\;& \sum_I\sum_{J=0}^{3}\langle L0J0|I0\rangle^2\Big\{\cos^2\gamma N_2(2-a_1)(2-a_2)r_1r_2\frac{1}{2}\Big[\\
&-(\delta_{J0}+\delta_{J1})F(N_1{-}1,N_2{-}1,I)
\end{aligned}
$$

$$
\begin{aligned}
&+(N_1{-}1)\frac{1}{3}((3a_1-1)\delta_{J0}+3\delta_{J1}+(4-3a_1)\delta_{J2})F(N_1{-}2,N_2{-}1,I)\\
&+(N_1{-}1)(N_1{-}2)a_1(2-a_1)\frac{1}{30}(5\delta_{J0}-3\delta_{J1}-5\delta_{J2}+3\delta_{J3})\\
&\qquad\times F(N_1{-}3,N2{-}1,I)\Big]\\
&+\cos\gamma\sin\gamma\sqrt{N_1N_2}\Big[((a_1a_2-a_1-a_2)\delta_{J0}+(2-a_1-a_2+a_1a_2)\delta_{J1})\\
&\qquad\times F(N_1{-}1,N_2{-}1,I)\\
&+\frac{1}{3}(N_1{-}1)(2-a_1)(1-a_2)a_1(-\delta_{J0}+\delta_{J2})F(N_1{-}2,N_2{-}1,I)\\
&+\frac{1}{3}(N_2{-}1)(2-a_2)(1-a_1)a_2(-\delta_{J0}+\delta_{J2})F(N_1{-}1,N_2{-}2,I)\\
&+\frac{1}{30}(N_1{-}1)(N_2{-}1)a_1(2-a_1)a_2(2-a_2)\\
&\qquad\times(5\delta_{J0}-3\delta_{J1}-5\delta_{J2}+3\delta_{J3})\,F(N_1{-}2,N_2{-}2,I)\Big]\\
&+\sin^2\gamma N_1(2-a_1)(2-a_2)r_1r_2\frac{1}{2}\Big[-(\delta_{J0}+\delta_{J1})F(N_1{-}1,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{3}((3a_2-1)\delta_{J0}+3\delta_{J1}+-(\delta_{J0}+\delta_{J1})F(N_1{-}1,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{3}((3a_2-1)\delta_{J0}+3\delta_{J1}+(4-3a_2)\delta_{J2})F(N_1{-}1,N_2{-}2,I)\\
&+(N_2{-}1)(N_2{-}2)a_2(2-a_2)\frac{1}{30}(5\delta_{J0}-3\delta_{J1}-5\delta_{J2}+3\delta_{J3})\\
&\qquad\times F(N_1{-}1,N_2{-}3,I)\Big]\Big\},
\end{aligned}
\tag{3.80}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot\hat{D}_2\rangle_L \;=\;& N_1N_2(2-a_1)(2-a_2)r_1r_2\\
&-(N_1\sin^2(\gamma)+N_2\cos^2(\gamma))(2-a_1)(2-a_2)r_1r_2\\
&-(N_1N_2)^{1/2}(1+a_1+a_2)\sin(2\gamma)\\
&+\frac{N_1^{1/2}N_2^{1/2}}{N}(\bar{a^2}N-2(N_1+N_2)a_1a_2)\sin(2\gamma)\\
&+\frac{N_1N_2}{N}(2-a_1)(2-a_2)r_1r_2(-3+2a_1+2a_2+(a_1-a_2)\cos(2\gamma))\\
&+\frac{\bar{L}}{N^2}\Big[N_1^{3/2}N_2^{1/2}(2-a_1)(1-a_2)a_1\sin(2\gamma)\\
&+N_1^{1/2}N_2^{3/2}(1-a_1)(2-a_2)a_2\sin(2\gamma)\\
&+N_1N_2(2-a_1)(2-a_2)r_1r_2(3-2a_1-2a_2-(a_1-a_2)\cos(2\gamma))\Big].
\end{aligned}
\tag{3.81}
$$

$$
\begin{aligned}
\langle M_4' \rangle_L \;=\; & \sum_I \sum_{J=0}^{4} \langle L0J0|I0\rangle^2 \Big\{ \cos^2\gamma N_2 \frac{1}{4}\Big[(2-a_1)(2-a_2)(1+r_1r_2)^2\delta_{J1} \\
& \times F(N_1{-}1, N_2{-}1, I) \\
& +(N_1{-}1)\frac{1}{12}\Big((2-a_1)\,(3a_1+a_2-3a_1a_2-(4-3a_1)(2-a_2)r_1r_2)\,(\delta_{J0}+2\delta_{J2}) \\
& +6\,(a_1(4+3a_1+a_2-a_1a_2)+(2-a_1)(2-a_2)(2-3a_1)r_1r_2)\,\delta_{J1}\Big) \\
& \times F(N_1{-}2, N_2{-}1, I) \\
& +(N_1{-}1)(N_1{-}2)\frac{1}{30}(2-a_1)^2a_1(2-a_2)(r_1-r_2)^2 \\
& \times (-5\delta_{J0}+12\delta_{J1}-10\delta_{J2}+3\delta_{J3})\,F(N_1{-}3, N_2{-}1, I)\Big] \\
& +\cos\gamma\sin\gamma\sqrt{N_1N_2}\frac{1}{2}(2-a_1)(2-a_2)\Big[-(1+r_1r_2)^2\delta_{J1}F(N_1{-}1, N_2{-}1, I) \\
& +(N_1 1)\frac{1}{6}(2-a_1)r_1(r_2-r_1)(1+r_1r_2)\,(\delta_{J0}-3\delta_{J1}+2\delta_{J2}) \\
& \times F(N_1{-}2, N_2{-}1, I) \\
& +(N_2{-}1)\frac{1}{6}(2-a_2)r_2(r_1-r_2)(1+r_1r_2)\,(\delta_{J0}-3\delta_{J1}+2\delta_{J2}) \\
& \times F(N_1{-}1, N_2{-}2, I) \\
& +(N_1{-}1)(N_2{-}1)\frac{1}{30}r_1r_2(r_1-r_2)^2\,(-5\delta_{J0}+12\delta_{J1}-10\delta_{J2}+3\delta_{J3}) \\
& \times F(N_1{-}2, N_2{-}2, I)\Big] \\
& +\sin^2\gamma N_1\frac{1}{4}\Big[(2-a_1)(2-a_2)(1+r_1r_2)^2\delta_{J1}F(N_1{-}1, N_2{-}1, I) \\
& +(N_2{-}1)\frac{1}{6}(2-a_1)(2-a_2)^2(r_1-r_2)\Big((3r_2-r_2^2r_1+r_1)\delta_{J0} \\
& 3r_2(2r_2-r_2^3++3r_2r_1)\delta_{J1} \\
& +(r_1-6r_2-4r_2^2r_1)\delta_{J2}\Big)F(N_1{-}1, N_2{-}2, I) \\
& +(N_2{-}1)(N_2{-}2)\frac{1}{30}(2-a_1)(2-a_2)^2a_2(r_1-r_2)^2 \\
& (-5\delta_{J0}+12\delta_{J1}-10\delta_{J2}+3\delta_{J3})\,F(N_1{-}1, N_2{-}3, I)\Big]\Big\}, \qquad (3.82)
\end{aligned}
$$

$$
\begin{aligned}
\langle M_4' \rangle_L \;=\; & \frac{1}{4}N_1N_2(2-a_1)(2-a_2)(r_1-r_2)^2\sin(2\gamma) \\
& +(N_1\sin^2(\gamma)+N_2\cos^2(\gamma))(2-a_1)(2-a_2)(1+r_1-r_2+r_1r_2) \\
& \times(1-r_1+r_2+r_1r_2) \\
& -\frac{1}{4}(N_1N_2)^{1/2}(2-a_1)(2-a_2)(1+r_1r_2)^2\sin(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{4N}N_1^{3/2}N_2^{1/2}(2-a_1)(a_1(2-a_1-a_1a_2)\\
&\quad -2r_1r_2(2-a_1)(2-a_2)(1-a_1))\sin(2\gamma)\\
&+\frac{1}{2N}N_1N_2(a_1+a_2-2)(2(a_1+a_2-a_1a_2)+(a_1-a_2)\cos(2\gamma))\\
&-\frac{1}{4N}N_1^{1/2}N_2^{3/2}(2-a_2)(a_2(2-a_2-a_1a_2)\\
&\quad -2r_1r_2(2-a_1)(2-a_2)(1-a_2))\sin(2\gamma)\\
&+\frac{\bar{L}}{4N^2}\Big[N_1^{1/2}N_2^{1/2}a_1a_2(N_1(2-a_1)+N_2(2-a_2))\sin(2\gamma)\\
&\quad +2N_1N_2(a_1+a_2-2)(2(a_1+a_2-a_1a_2)+(a_1-a_2)\cos(2\gamma))\Big]. \qquad (3.83)
\end{aligned}
$$

In considering the variation of γ using only the first layer, note that the form of the equation is

$$
\begin{aligned}
E &= c_1\cos(2\gamma)+c_2\sin(2\gamma)+c_3\cos^2(\gamma)+c_4\sin^2(\gamma)\\
&= \frac{1}{2}(2c_1+c_3-c_2)\cos(2\gamma)+c_4\sin(2\gamma), \qquad (3.84)
\end{aligned}
$$

where the c_i's are functions of the Hamiltonian parameters. Substituting $g = \cos(2\gamma)$ and differentiating with respect to this parameter gives the following solution

$$
g = \pm\frac{2c_1+c_3-c_2}{[(2c_1+c_3-c_2]^{1/2}+4c_4^2]^{1/2}}. \qquad (3.85)
$$

3.4.2 Antisymmetric Stretching

It is clear from the form of the wavefunctions (3.58,3.59) that the equivalent antisymmetric stretching results may be obtained from the symmetric calculations by making the substitutions $\cos\gamma \rightarrow \sin\gamma$ and $\sin\gamma \rightarrow -\cos\gamma$. These calculations are therefore not repeated here.

3.4.3 Bending

As previously indicated, one of these states is a spurious one representing a rotation of the ground state. This is most simply incorporated within the formalism by ensuring that the normalization of the spurious state vanishes. This provides a criteria by which the parameter γ can be determined for use in the antisymmetric bending state.

The bending calculations are distinct from the other $1/N$ expansion ones that have been presented here in that the projection on to the body-fixed axis has $K = 1$

rather than $K = 0$ as has been the case for the other calculations. In this case the normalization is given by [5]

$$\begin{aligned}
\mathcal{N}_S &= \frac{2L+1}{2}\int_0^\pi d\beta \sin\beta d^L_{11}(\beta)\frac{1}{N_1!N_2!} \\
&\quad \times\langle 0|[\sqrt{N_1}\cos\gamma b''_1(b_1)^{N_1-1}(b_2)^{N_2} + \sqrt{N_2}\sin\gamma(b_1)^{N_1}b''_2(b_2)^{N_2-1}] \\
&\quad \times[\sqrt{N_1}\cos\gamma b''^{\dagger}_{1R}(b^{\dagger}_{1R})^{N_1-1}(b^{\dagger}_{2R})^{N_2} + \sqrt{N_2}\sin\gamma(b^{\dagger}_{1R})^{N_1}b''^{\dagger}_{2R}(b^{\dagger}_{2R})^{N_2-1}]|0\rangle \\
&= \frac{2L+1}{2}\int_0^\pi d\beta \sin\beta d^L_{11}(\beta)\Big\{\cos^2\gamma\Big[d^1_{11}Z_1^{N_1-1} \\
&\quad +\frac{1}{2}(N_1-1)x^2_{1,1}(-d^1_{11}+d^2_{11})Z_1^{N_1-2}\Big]Z_2^{N_2} \\
&\quad +\cos\gamma\sin\gamma x_{1,1}x_{2,1}(-d^1_{11}+d^2_{11})Z_1^{N_1-1}Z_2^{N_2-1} \\
&\quad +\sin^2\gamma\Big[d^1_{11}Z_2^{N_2-1}+\frac{1}{2}(N_2-1)x^2_{2,1}(-d^1_{11}+d^2_{11})Z_2^{N_2-2}\Big]Z_1^{N_1}\Big\} \\
&= \sum_I\sum_{l=1}^{2}\Big\{\cos^2\gamma\Big[\delta_{l1}F(N_1-1,N_2,I) \\
&\quad +\frac{1}{2}(N_1-1)x^2_{1,1}(-\delta_{l1}+\delta_{l2})F(N_1-2,N_2,I)\Big] \\
&\quad +\cos\gamma\sin\gamma x_{1,1}x_{2,1}(-\delta_{l1}+\delta_{l2})F(N_1-1,N_2-1,I) \\
&\quad +\sin^2\gamma\Big[\delta_{l1}F(N_1,N_2-1,I)+\frac{1}{2}(N_2-1)x^2_{2,1}(-\delta_{l1}+\delta_{l2})F(N_1,N_2-2,I)\Big] \\
&\quad \times\langle L11-1|I0\rangle^2 \\
&= 1-\frac{1}{N}(a_1N_1\cos^2\gamma+2[a_1N_1a_2N_2]^{1/2}\cos\gamma\sin\gamma+a_2N_2\sin^2\gamma). \qquad (3.86)
\end{aligned}$$

where the expansion given here includes only the leading order terms. On requiring this to vanish, the following conditions are obtained

$$\cos\gamma=\sqrt{\frac{a_1N_1}{N}},\quad \sin\gamma=\sqrt{\frac{a_2N_2}{N}}. \qquad (3.87)$$

These substitutions are used in the subsequent calculations dealing with the antisymmetric bending state.

The normalization of the (antisymmetric) bending state can be obtained from the spurious one through the substitutions (as in the case of the stretching states) $\cos\gamma\rightarrow\sin\gamma$ and $\sin\gamma\rightarrow-\cos\gamma$, giving

$$\begin{aligned}
\mathcal{N}_A &= \sum_I\sum_{l=1}^{2}\Big\{\sin^2\gamma\Big[\delta_{l1}F(N_1-1,N_2,I) \\
&\quad +\frac{1}{2}(N_1-1)x^2_{1,1}(-\delta_{l1}+\delta_{l2})F(N_1-2,N_2,I)\Big] \\
&\quad -\cos\gamma\sin\gamma x_{1,1}x_{2,1}(-\delta_{l1}+\delta_{l2})F(N_1-1,N_2-1,I) \\
&\quad +\cos^2\gamma\Big[\delta_{l1}F(N_1,N_2-1,I)+\frac{1}{2}(N_2-1)x^2_{2,1}(-\delta_{l1}+\delta_{l2})F(N_1,N_2-2,I)\Big] \\
&\quad \times\langle L11-1|I0\rangle^2. \qquad (3.88)
\end{aligned}$$

The $1/N$ expansion is obtained as usual and substituting Eq. (3.87) for $\cos\gamma$ and $\sin\gamma$, gives

$$\begin{aligned}\mathcal{N}_A &= 1+\frac{1}{N^2}(a_1N_1(2a_2-a_1)+a_2N_2(2a_1-a_2))\\ &\quad -\frac{\bar{L}}{N}\left[1+\frac{1}{N^2}(a_1N_1(4a_2-3a_1)+a_2N_2(4a_1-3a_2))\right]\\ &\quad +\frac{\bar{L}^2}{2N^2}\left[1+\frac{2}{3N^2}(a_1N_1(1-9a_1+9a_2)+a_2N_2(1+9a_1-9a_2))\right]\\ &\quad -\frac{\bar{L}^3}{6N^3}\left[1+\frac{2}{N^2}(a_1N_1(5a_1-4a_2-1)+a_2N_2(5a_2-4a_1-1))\right]\\ &\quad +\frac{\bar{L}^4}{24N^4}. \end{aligned} \tag{3.89}$$

The expectation values of various terms in the Hamiltonian in the bending state are presented next. The substitutions for $\cos\gamma$ and $\sin\gamma$ obtained above will not be applied until the last stage of each calculation. The matrix elements involved in the calculation of operator expectation values are the same as those presented in the symmetric stretching section, save that b_i' is replaced by b_i'', and $\cos\gamma$ and $\sin\gamma$ are replaced as already described. These change the form of the calculation enough to warrant giving new results for the stage prior to substitution of the normalization term. As before, the relevant operator derivatives are given in Appendix E.

$$\begin{aligned}\langle\hat{n}_{p1}\rangle_L &= \sum_I\sum_{J=0}^{4}\langle L1J-1|I0\rangle^2\Big\{\sin^2\gamma\Big[\delta_{J1}F(N_1{-}1,N_2,I)\\ &\quad -\frac{1}{4}(N_1{-}1)a_1(\delta_{J1}-3\delta_{J2})F(N_1{-}2,N_2,I)\\ &\quad -\frac{1}{120}(N_1{-}1)(N_1{-}2)a_1^2(3\delta_{J0}+5\delta_{J1}-8\delta_{J2})F(N_1{-}3,N_2,I)\Big]\\ &\quad +\cos\gamma\sin\gamma[N_1N_2a_1a_2]^{1/2}\frac{1}{2}\Big[-(\delta_{J1}-\delta_{J2})F(N_1{-}1,N_2{-}1,I)\\ &\quad -\frac{1}{15}(N_1{-}1)a_1(3\delta_{J1}+5\delta_{J2}-8\delta_{J3})F(N_1{-}2,N_2{-}1,I)\Big]\\ &\quad +\cos^2\gamma N_1a_1\frac{1}{4}\Big[(\delta_{J1}+\delta_{J2})F(N_1{-}1,N_2{-}1,I)\\ &\quad -\frac{1}{15}(N_2{-}1)a_2(3\delta_{J1}+5\delta_{J2}-8\delta_{J3})F(N_1{-}1,N_2{-}2,I)\Big]\Big\}, \end{aligned} \tag{3.90}$$

$$\begin{aligned}\langle\hat{n}_{p1}\rangle_L &= \frac{N_1a_1}{2}-\frac{1}{2N}(N_1a_1(2-a_1)-N_2a_2)+\frac{1}{2N}N_2a_2(2-a_1)\\ &\quad +\frac{2}{N^2}N_2a_1a_2(2-a_1)+\frac{1}{N^3}N_1^2a_1^2(2-a_1+a_1^2-4a_2+2a_1a_2+3a_2^2)\\ &\quad +\frac{1}{N^3}N_1N_2(-10a_1+8a_1^2+2a_2-a_1a_2)\end{aligned}$$

$$
\begin{aligned}
&+\frac{1}{N^4}N_1a_1\Big[N_1^2a_1^2(2a_1-a_1^2+2a_2-3a_1a_2-2a_2^2)\\
&+N_1N_2a_1a_2(4a_1-7a_1^2+4a_2-5a_2^2)+N_2^2a_2(2-3a_1)(a_1+a_2)\Big]\\
&+\frac{1}{N^5}N_1a_2^2\Big[N_1^3a_1^2(-a_1+2a_2)+N_1^2N_2a_1a_2(-a_1^2+3a_1a_2+a_2^2)+\\
&N_1N_2^2a_2^2(a_1^2+3a_1a_2-a_2^2)+N_2^3a_2^3(2-a_1-a_2)\Big]\\
&+\frac{\bar{L}}{N^2}\Big\{N_1(2-a_1)a_1-\frac{2}{N}N_2a_1a_2(2-a_1)\\
&+\frac{1}{N^2}\Big[N_1^2a_1^2(1+4a_1-2a_1^2+8a_2-4a_1a_2-6a_2^2)\\
&+N_1N_2a_1a_2(1+20a_1-16a_1^2-6a_2+3a_1a_2)\\
&+N^2N_1^2(2-a_1)a_1a_2^2\Big]\\
&+\frac{1}{N^3}\Big[N_1^3a_1^3(-9a_1+3a_1^2-4a_2+8a_1a_2+4a_2^2)\\
&+N_1^2N_2a_1^2a_2(-13a_1+20a_1^2-13a_2-5a_1a_2+15a_2^2)\\
&+N_1N_2^2a_1a_2^2(-4a_1+6a_1^2-9a_2+9a_1a_2)\\
&+\frac{1}{N^4}N_1a_1^2a_2\Big[N_1^3a_1^2(3a_1-4a_2)+N_1^2N_2a_1(3a_1^2-5a_1a_2-a_2^2)\\
&+N_1N_2^2a_2(-a_1^2-5a_1a_2+3a_2^2)\\
&+N_2^3a_2^2(-4a_1+3a_2)\Big]\Big\}\\
&+\frac{\bar{L}^2}{6N^4}\Big\{N_2(2-a_1)a_2+\frac{1}{N}\Big[N_1^2a_1^2(-14-2a_1+3a_1^2-4a_2+6a_1a_2+9a_2^2)\\
&+N_1N_2a_1a_2(-16-17a_1+24a_1^2+12a_2-6a_1a_2)-N_2^2a_2^2(2-a_1)\Big]\\
&+\frac{1}{N^2}\Big[2N_1^3a_1^3(1+12a_1-3a_1^2+4a_2-9a_1a_2-6a_2^2)\\
&+N_1^2N_2a_1^2a_2(4+31a_1-51a_1^2+33a_2+18a_1a_2-39a_2^2)\\
&+N_1N_2^2a_1a_2^2(2+7a_1-18a_1^2+25a_2-18a_1a_2)\Big]\\
&+\frac{1}{N^5}N_1N_2a_1a_2\Big[N_1^2a_1^2(2a_1-15a_1^2+7a_2+9a_1a_2-3a_2^2)\\
&+N_1N_2a_1a_2(7a_1-3a_1^2+2a_2+9a_1a_2-15a_2^2)\\
&+N_2^2a_2^2(4a_1+12a_1-a_{@}-15a_1a_2)\Big]\Big\}. \qquad (3.91)
\end{aligned}
$$

$$
\begin{aligned}
\langle\hat{n}_{p1}^2\rangle_L \;=\; &\sum_I\sum_{J=0}^{4}\langle L1J-1|I0\rangle^2\Big\{\sin^2\gamma\Big[\delta_{J1}F(N_1{-}1,N_2,I)\\
&+(N_1{-}1)\frac{1}{4}a_1\,(-\delta_{J1}+7\delta_{J2})\,F(N_1{-}2,N_2,I)
\end{aligned}
$$

$$
\begin{aligned}
&+(N_1{-}1)(N_1{-}2)\frac{1}{40}a_1^2\,(-\delta_{J1}-5\delta_{J2}+16\delta_{J3})\,F(N_1{-}3,N_2,I)\\
&+(N_1{-}1)(N_1{-}2)(N_1{-}3)\frac{1}{1680}a_1^3\,(-21\delta_{J1}+5\delta_{J2}-14\delta_{J3}+30\delta_{J4})\\
&\qquad\times F(N_1{-}4,N_2,I)\Big]\\
&+\cos\gamma\sin\gamma[N_1N_2a_1a_2]^{1/2}\frac{1}{4}\Big[(-\delta_{J1}+\delta_{J2})\,F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{10}a_1\,(-3\delta_{J1}-5\delta_{J2}+8\delta_{J3})\,F(N_1{-}2,N_2{-}1,I)\\
&+(N_1{-}1)(N_1{-}2)\frac{1}{420}a_1^2\,(-21\delta_{J1}+5\delta_{J2}-14\delta_{J3}+30\delta_{J4})\,F(N_1{-}3,N_2{-}1,I)\Big]\\
&+\cos^2\gamma N_1\frac{1}{4}a_1\Big[(\delta_{J1}+\delta_{J2})\,F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{15}a_1\,(6\delta_{J1}+5\delta_{J2}+4\delta_{J3})\,F(N_1{-}2,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{40}a_2\,(-3\delta_{J1}+5\delta_{J2}+8\delta_{J3})\,F(N_1{-}1,N_2{-}2,I)\\
&+(N_1{-}1)(N_2{-}1)\frac{1}{420}a_1a_2\,(-21\delta_{J1}+5\delta_{J2}-14\delta_{J3}+30\delta_{J4})\\
&\qquad\times F(N_1{-}2,N_2{-}2,I)\Big]\Big\}
\end{aligned}
\tag{3.92}
$$

$$
\begin{aligned}
\langle\hat{n}_{p1}^2\rangle_L \;=\;& \frac{N_1^2a_1^2}{4}+\frac{1}{4}N_1a_1(2-a_1)+\frac{N_1}{2N}a_1(2-a_1)(N_2a_2-N_1a_1)\\
&-\frac{N_1^2}{2N^2}(N_1+N_2)a_1^3a_2+\frac{1}{2}(2-3a_1+a_1^2)\\
&-\frac{1}{2N}N_1a_1(12-22a_1+10a_1^2)\\
&+\frac{1}{2N^2}N_1^2a_1^2(16-24a_1-8a_2+3a_1^2+5a_2^2-a_1a_2)\\
&+\frac{1}{2N^3}N_1^2N_2a_1^2a_2(-12a_1+12a_2+15a_1^2-5a_2^2-6a_1a_2)\\
&+\frac{1}{N^4}N_1^3a_1^4a_2(N_1a_2+N_2(3a_2-a_1))\\
&+\frac{\bar{L}}{2N^2}\Big[N_1^2a_1^2(2-a_1)+N_1a_1(10-15a_1+5a_1^2)\\
&-\frac{1}{N}N_1^2a_1^2(15+13a_1-8a_2+4a_1^2+6a_2^2-5a_1a_2)\\
&+\frac{1}{N^2}N_1^2N_2a_1^2a_2(45a_1-35a_2-22a_1^2+6a_2^2+16a_1a_2)\\
&+\frac{1}{N^3}N_1^3N_2a_1^3a_2(18(a_1^2+a_2^2)-34a_1a_2)\Big]\\
&+\frac{\bar{L}^2}{12N^3}N_1a_1\Big[2(2-a_1)-\frac{1}{N}N_1a_1(6-18a_1-8a_2+3a_1^2-9a_2^2+27a_1a_2)
\end{aligned}
$$

$$+\frac{1}{N^2}N_1N_2a_1a_2(52(a_2-a_1)+33a_1^2-9a_2^2-24a_1a_2)$$
$$+\frac{1}{N^3}54N_1^2N_2a_1^2a_2(2a_1a_2-a_1^2-a_2^2)\Big]. \tag{3.93}$$

$$\begin{aligned}\langle\hat{n}_{p1}\hat{n}_{p2}\rangle_L &= \sum_I\sum_{J=0}^{4}\langle L1J-1|I0\rangle^2\Big\{\sin^2\gamma N_b\frac{1}{4}a_2\Big[(\delta_{J1}+\delta_{J2})\,F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{5}a_1\,(\delta_{J1}+4\delta_{J3})\,F(N_1{-}2,N_2{-}1,I)\\
&+(N_1{-}1)(N_1{-}2)\frac{1}{420}a_1^2\,(-21\delta_{J1}+5\delta_{J2}-14\delta_{J3}+30\delta_{J4})\\
&\qquad\times F(N_1{-}3,N_2{-}1,I)\Big]\\
&+\cos\gamma\sin\gamma[N_1N_2a_1a_2]^{1/2}\frac{1}{4}\Big[(-\delta_{J1}+\delta_{J2})\,F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{30}a_1\,(-3\delta_{J1}-5\delta_{J2}+8\delta_{J3})\,F(N_1{-}2,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{30}a_2\,(-3\delta_{J1}-5\delta_{J2}+8\delta_{J3})\,F(N_1{-}1,N_2{-}2,I)\\
&+(N_1{-}1)(N_2{-}1)\frac{1}{420}a_1a_2\,(-21\delta_{J1}+5\delta_{J2}-14\delta_{J3}+30\delta_{J4})\\
&\qquad\times F(N_1{-}2,N_2{-}2,I)\Big]\\
&+\cos^2\gamma N_1\frac{1}{4}a_1\Big[(\delta_{J1}+\delta_{J2})\,F(N_1{-}1,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{5}a_2\,(\delta_{J1}+4\delta_{J3})\,F(N_1{-}1,N_2{-}2,I)\\
&+(N_2{-}1)(N_2{-}2)\frac{1}{420}a_2^2\,(-21\delta_{J1}+5\delta_{J2}-14\delta_{J3}+30\delta_{J4})\\
&\qquad\times F(N_1{-}1,N_2{-}3,I)\Big]\Big\},\end{aligned} \tag{3.94}$$

$$\begin{aligned}\langle\hat{n}_{p1}\hat{n}_{p2}\rangle_L &= \frac{1}{4}N_1N_2a_1a_2+\frac{1}{4N}(a_1N_1-a_2N_2)(a_1N_1(2-a_2)-a_2N_2(2-a_1))\\
&-\frac{1}{4}(4-2a_1-2a_2+a_1a_2)+\frac{1}{N^2}N_1N_2a_1a_2(4+2a_1+2a_2-a_1^2-a_2^2-2a_1a_2)\\
&+\frac{3}{N^3}N_1N_2a_1^2a_2^2(2(N_1+N_2)+(a_2N_1+a_1N_2))-\frac{3}{2N^4}(N_1N_2a_1a_2)^2(a_1^2+a_2^2)\\
&+\frac{1}{2N^5}N_1^2N_2^2a_1a_2(a_1^3N_1+a_2^3N_2-3a_1a_2(a_2N_1+a_1N_2))\\
&+\frac{\bar{L}}{2N^2}a_1a_2\Big[\frac{1}{2}N_1N_2(4-a_1-a_2)+N_1(2-a_2)+N_2(2-a_1)\\
&-\frac{1}{N}N_1N_2(7+8(a_1+a_2)+3(a_1^2+a_2^2)+11a_1a_2)\\
&+\frac{1}{N^2}N_1N_2(28a_1a_2(N_1+N_2)-18a_1a_2(a_2N_1+a_1N_2)-\bar{a}^3N)\end{aligned}$$

$$
\begin{aligned}
&-\frac{1}{N^3}N_1N_2a_1a_2(7(a_1+a_2)-21(a_1^2+a_2^2)+30a_1a_2)\\
&+\frac{1}{N^4}N_1N_2a_1a_2(a_2N_1+a_1N_2)\Big]\\
&+\frac{\bar{L}^2}{12N^2}\Big[-2+\frac{1}{N}a_1a_2(N_1+N_2)\\
&+\frac{1}{N^2}N_1N_2a_1a_2(2+40(a_1+a_2)-3(a_1^2+a_2^2)-36a_1a_2)\\
&+\frac{1}{N^3}N_1N_2a_1^2a_2^2(N_1(21a_2-50)+N_2(21a_1-50))\\
&+\frac{1}{N^4}(N_1N_2a_1a_2)^2(28(a_1+a_2)-42(a_1^2+a_2^2+93a_1a_2)\Big].
\end{aligned}
\tag{3.95}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot\hat{D}_1\rangle_L \;=\; &\sum_I\sum_{J=0}^{4}\langle L1J-1|I0\rangle^2\Big\{\sin^2\gamma\Big[\delta_{J1}F(N_1{-}1,N_2,I)\\
&+(N_1{-}1)\frac{1}{4}\left((20-11a_1)\delta_{J1}+3a_1\delta_{J2}\right)F(N_1{-}2,N_2,I)\\
&+(N_1{-}1)(N_1{-}2)\frac{1}{60}a_1\left(3(2a_1-5)\delta_{J1}+5(27-14a_1)\delta_{J2}+4a_1\delta_{J3}\right)\\
&\qquad\times F(N_1{-}3,N_2,I)\\
&+(N_1{-}1)(N_1{-}2)(N_1{-}3)\frac{1}{60}a_1^2(2-a_1)\left(9\delta_{J1}-5\delta_{J2}-4\delta_{J3}\right)F(N_1{-}4,N_2,I)\Big]\\
&+\cos\gamma\sin\gamma[N_1N_2a_1a_2]^{1/2}\frac{1}{4}\Big[(\delta_{J2}-\delta_{J1})F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{15}\left(3(12a_1-25)\delta_{J1}+5(15-8a_1)\delta_{J2}+4a_1\delta_{J3}\right)F(N_1{-}2,N_2{-}1,I)\\
&+(N_1{-}1)(N_1{-}2)\frac{1}{15}(2-a_1)a_1\left(9\delta_{J1}-5\delta_{J2}-4\delta_{J3}\right)F(N_1{-}3,N_2,I)\Big]\\
&+\cos^2\gamma N_1\frac{1}{4}\Big[\left((12-5a_1)\delta_{J1}+a_1\delta_{J2}\right)F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)(2-a_1)a_1\left(3\delta_{J1}+\delta_{J2}\right)F(N_1{-}2,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{15}a_2\left(3(7a_1-15)\delta_{J1}+5(9-5a_1)\delta_{J2}+4a_1\delta_{J3}\right)F(N_1{-}1,N_2{-}2,I)\\
&+(N_1{-}1)(N_2{-}1)\frac{1}{15}(2-a_1)a_1a_2\left(-9\delta_{J1}+5\delta_{J2}+4\delta_{J3}\right)\\
&\qquad\times F(N_1{-}2,N_2{-}2,I)\Big]\Big\},
\end{aligned}
\tag{3.96}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot\hat{D}_1\rangle_L \;=\; &N_1^2(2-a_1)+N_1(1-a_1)(2-a_1)\\
&+\frac{N_1}{N}(N_2a_2-N_1a_1)(2-a_1)(1-2a_1)-2(2-a_1)(1-a_1)\\
&+\frac{2}{N}N_1a_1(2-a_1)(5-6a_1)
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{2}{N^2}N_1^2a_1(-9a_1+5a_2+10a_1^2-14a_1a_2-3a_1^3+6a_1^2a_2)\\
&+\frac{2}{N^3}N_1^3a_2(6a_1-6a_2-21a_1^2+6a_2^2+15a_1a_2+9a_1^3-6a_1^2a_2-3a_1a_2^2)\\
&-\frac{12}{N^4}N_1^3N_2a_1^2a_2(2-a_1)(a_1^2+a_2^2+a_1a_2)\\
&+\frac{\bar{L}}{N^2}\Big[N_1^2a_1(2-a_1)(1-2a_1)+2N_1a_1(2-a_1)(4-5a_1)\\
&+\frac{2}{N}N_1^2a_1(2+19a_1-30a_2-46a_1^2+71a_1a_2+18a_1^3-30a_1^2a_2)\\
&+\frac{2}{N^2}N_1^3a_1^2(-14a_1+14a_2+55a_1^2-20a_2^2-35a_1a_2-24a_1^3-56a_2^3+50a_1^2a_2\\
&\qquad -72a_1a_2^2-18a_1^3a_2+28a_1a_2^3+41a_1^2a_2^2)\\
&+\frac{2}{N^3}N_1^3N_2a_1^2a_2(2-a_1)(18a_1^2-28a_2^2-41a_1a_2)\Big]\\
&+\frac{\bar{L}^2}{3N^4}N_1^2a_1\Big[-18+13a_1+24a_2+58a_1^2-126a_1a_2-30a_1^3+51a_1^2a_2\\
&+\frac{1}{N}N_1a_1(32a_1-8a_2-82a_1^2+18a_2^2+64a_1a_2+33a_1^3-24a_1^2a_2-9a_1a_2^2)\\
&+\frac{54}{N^2}N_1N_2a_1a_2(2-a_1)(2a_1a_2-a_1^2a_2^2)\Big],
\end{aligned}
\tag{3.97}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot\hat{D}_2\rangle_L &= \sum_I\sum_{J=0}^{4}\langle L1J-1|I0\rangle^2(2-a_1)(2-a_2)r_1r_2\frac{1}{60}\Big\{\\
&\sin^2\gamma(N_1-1)N_2\Big[30(\delta_{J1}+\delta_{J2})F(N_1-2,N_2-1,I)\\
&\qquad+(N_1-2)a_1(-\delta_{J1}+5\delta_{J2}+4\delta_{J3})F(N_1-3,N_2-1,I)\Big]\\
&+\cos\gamma\sin\gamma\left[\frac{N_1N_2}{a_1a_2}\right]^{1/2}\frac{1}{2}\Big[60\delta_{J1}F(N_1-1,N_2-1,I)\\
&\qquad+15(N_1-1)a_1(\delta_{J1}+\delta_{J2})F(N_1-2,N_2-1,I)\\
&\qquad+15(N_2-1)a_2(\delta_{J1}+\delta_{J2})F(N_1-1,N_2-2,I)\\
&\qquad+2(N_1-1)(N_2-1)a_1a_2(-\delta_{J1}+10\delta_{J2}+8\delta_{J3})F(N_1-2,N_2-2,I)\Big]\\
&+\cos^2\gamma N_1(N_2-1)\frac{1}{4}\Big[30(\delta_{J1}+\delta_{J2})F(N_1-1,N_2-2,I)\\
&\qquad+(N_2-2)a_2((-\delta_{J1}+5\delta_{J2}+4\delta_{J3})F(N_1-1,N_2-3,I)\Big]\Big\},
\end{aligned}
\tag{3.98}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot\hat{D}_2\rangle_L &= (2-a_1)(2-a_2)r_1r_2\Big\{N_1N_2\\
&-\frac{1}{N}(N_1^2a_1+N_1N_2(2-a_1-a_2)+N_2^2a_2)
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{N^2}\Big[(a_1^2N_1^2+a_2^2N_2^2)(2-a_1-a_2)-3a_1a_2(N_1+N_2)^2\\
&+\frac{2}{N}a_1a_2(a_1N_1^3+N_1^2N_2(7a_2-3)+N_1N_2^2(7a_1-3)+a_2N_2^3)\\
&+\frac{4}{N^2}N_1^2N_2^2a_1a_2(7a_1a_2-3a_1^2-3a_2^2)\Big]\\
&+\frac{\bar{L}}{N_3}\Big[N_1N_2(N_1+N_2)2a_1a_2+2(N_1+N_2)N(a_1+a_2-2)\\
&+2\Big(3a_1a_2(N_1^2+N_2^2)+N_1N_2(1+3a_1+3a_2-2a_1^2-2a_2^2+6a_1a_2)\Big)\\
&+\frac{2}{N}\Big(a_1a_2N_1N_2(N_1(1-2a_2)+N_2(1-2a_1))-N_1^3a_1^2a_2-N_2^3a_1a_2^2\Big)\\
&+\frac{2}{N^2}\Big(N_1N_2a_1a_2(-4a_1-4a_2+19a_1^2+19a_2^2-38a_1a_2)\\
&\qquad+N_1^2a_1^3(a_1-4)+N_2^2a_2^3(a_2-4)\Big)\Big]\\
&-\frac{\bar{L}^2}{3N^2}\Big[1+\frac{1}{N^2}N_1N_2(8-6(a_1+a_2)+3(a_1^2+a_2^2)+34a_1a_2)\\
&-\frac{1}{N^3}\Big(N_1^2N_2a_1(2a_1+21a_2^2-2a_2)+N_1N_2^2a_2(2a_2+21a_1^2-2a_1)+12\bar{a^2}N\Big)\\
&-\frac{1}{N^4}54N_1N_2a_1a_2(2a_1a_2-(a_1^2+a_2^2))\Big]\Big\},
\end{aligned}
\tag{3.99}
$$

$$
\begin{aligned}
\langle M_4'\rangle_L \;=\; &\sum_I\sum_{J=0}^{4}\langle L1J-1|I0\rangle^2\Big\{\sin^2\gamma N_2\frac{1}{2}\Big[(2-a_2)\delta_{J1}F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{2}\left((a_2-a_1)\delta_{J1}+(3a_1+a_2-2a_1a_2-(2-a_1)(2-a_2)r_1r_2)\delta_{J2}\right)\\
&\quad\times F(N_1{-}2,N_2{-}1,I)\\
&+(N_1{-}1)(N_1{-}2)\frac{1}{60}a_1(a_1a_2-a_1-a_2+(2-a_1)(2-a_2)r_1r_2)\\
&\quad\times(3\delta_{J1}+5\delta_{J2}-8\delta_{J3})\,F(N_1{-}3,N_2{-}1,I)\Big]\\
&+\cos\gamma\sin\gamma[N_1N_2(2-a_1)(2-a_2)]^{1/2}\frac{1}{2}\Big[-\delta_{J1}F(N_1{-}1,N_2{-}1,I)\\
&+(N_1{-}1)\frac{1}{4}\left(a_1-2r_1r_2+a_1r_1r_2\right)(\delta_{J1}-\delta_{J2})\,F(N_1{-}2,N_2{-}1,I)\\
&+(N_2{-}1)\frac{1}{4}\left(a_2-2r_1r_2+a_2r_1r_2\right)(\delta_{J1}-\delta_{J2})\,F(N_1{-}1,N_2{-}2,I)\\
&+(N_1{-}1)(N_2{-}1)\frac{1}{60}\left(a_1a_2(1+r_1r_2)-r_1r_2(a_1+a_2)\right)(3\delta_{J1}+5\delta_{J2}-8\delta_{J3})\\
&\quad\times F(N_1{-}2,N_2{-}2,I)\Big]\\
&+\cos^2\gamma N_1\frac{1}{2}\Big[(2-a_1)\delta_{J1}F(N_1{-}1,N_2{-}1,I)
\end{aligned}
$$

$$+(N_2{-}1)\frac{1}{2}\left((a_1-a_2)\delta_{J1}+(3a_2+a_1-2a_1a_2-2(2-a_1)(2-a_2)r_1r_2)\delta_{J2}\right)$$
$$\times F(N_1{-}1,N_2{-}2,I)$$
$$+(N_2{-}1)(N_2{-}2)\frac{1}{60}a_2\left(a_1a_2-a_1-a_2+(2-a_1)(2-a_2)r_1r_2\right)$$
$$\times\left(3\delta_{J1}+5\delta_{J2}-8\delta_{J3}\right)F(N_1{-}1,N_2{-}3,I)\Big]\Big\}, \tag{3.100}$$

$$\begin{aligned}\langle\hat{M}_4'\rangle_L &= \frac{1}{2}N_1N_2(a_1+a_2-a_1a_2-(2-a_1)(2-a_2)r_1r_2)\\ &+\frac{N_1^2}{2N}a_1(2-a_2)(1-a_1+(2-a_1)r_1r_2)+\frac{N_2^2}{2N}a_2(2-a_1)(1-a_2+(2-a_2)r_1r_2)\\ &+\frac{N_1N_2}{2N}[(a_1+a_2-2)(a_1+a_2-a_1a_2)-(a_1+a_2)(2-a_1)(2-a_2)r_1r_2]\\ &+\frac{\bar{L}}{2N^2}N_1N_2(a_1+a_2-2)(a_1+a_2-a_1a_2-(2-a_1)(2-a_2)r_1r_2).\end{aligned} \tag{3.101}$$

3.5 Applications to Molecular Spectra

The results obtained in the preceding sections allow systematic studies of triatomic molecules similar to those carried out for diatomic molecules in the last chapter. Available spectroscopic data on triatomic molecules are mostly concerned with the vibrational overtones. Data on rotational bands built on top of these overtones are mostly limited to the $L(L{+}1)$ term. Since the most interesting information on symmetry breaking effects come from the higher order terms (e.g. $(L(L{+}1))^2$), a detailed analysis of the moment of inertia systematics in triatomic molecules cannot be given. Therefore, systematic studies in this section will focus on the symmetry breaking effects on the first overtones.

Similarly, previous dynamical symmetry studies of triatomic molecules have been concerned with vibrational state excitation energies. This section shows how the impact of symmetry breaking terms on these results may be analyzed. For simplicity, a symmetric XY_2 molecule is considered, where it is assumed that $N_1 = N_2 = N, \kappa_1 = \kappa_2 = \kappa, \ldots$, and all Hamiltonian parameters are scaled by κ_{12}.

Figure 3.1 considers a case where $N = 100, \kappa' = \kappa/\kappa_{12} = 1$, and $\lambda_4' = \lambda_4/(4\kappa_{12})$ is varied from -0.3 to 0.3. All other Hamiltonian parameters are zero. Note that $\lambda_4' = 0$ corresponds to the local-mode limit in which the symmetric and anti-symmetric stretching energies are degenerate. The addition of the Majorana operator splits these two levels, varying the antisymmetric excitation energy proportionally to λ_4' and leaving the symmetric energy unaffected. The excitation energy of the bending mode is also proportional to λ_4'. As the bending mode is always lower than either

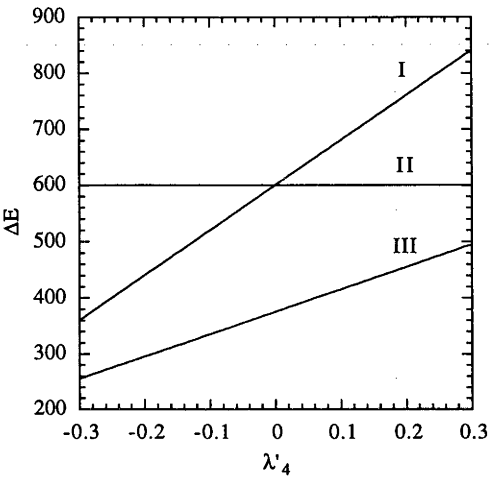

Figure 3.1: The effect of the Majorana symmetry breaking term with strength parameter λ'_{12} on the excitation energy ΔE. Shown are the (I) anti-symmetric stretching, (II) symmetric stretching, and (III) bending modes.

of the stretching modes, this result indicates that λ_4' cannot be made too large. However, it can be used to explain small energy splitting between the stretching modes observed in some XY_2 molecules.

The transition from local to normal mode is studied in Figure 3.2. In this figure $N = 100, \kappa' = (1-\zeta), \lambda' = \zeta$, and ζ is varied from 0 to 1. In this case the excitation energy of the bending mode is unaffected, as the contributions of the two varying terms are equal (at least to first order). However, the degeneracy of the stretching modes is removed, and both excitations decrease with ζ.

Figure 3.3 examines the influence of adding the $\sigma_{12}' = \sigma_{12}/(4\kappa_{12})$ term to a local-mode Hamiltonian with $N = 100$ and $\kappa' = 1$. The degeneracy of the stretching modes is again split. However, the difference between the stretching and bending mode excitations is roughly maintained. Thus it could be a useful scale parameter in systems where this occurs.

These figures show how the analytical results provided by the $1/N$ expansion may be used to determine parameter ranges that will best describe specific features of realistic spectra.

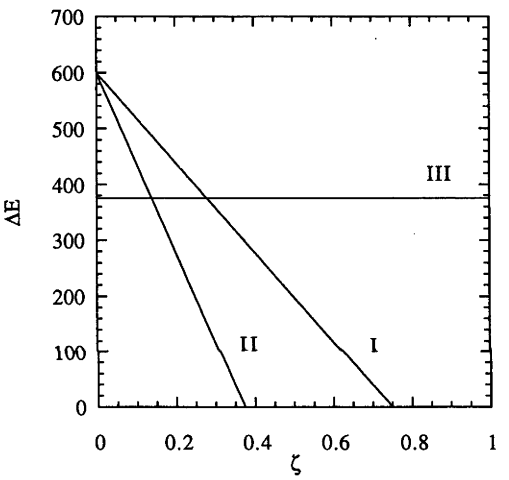

Figure 3.2: The transition from local ($\zeta = 0$) to normal mode ($\zeta = 1$) excitation energies. I-III are as before.

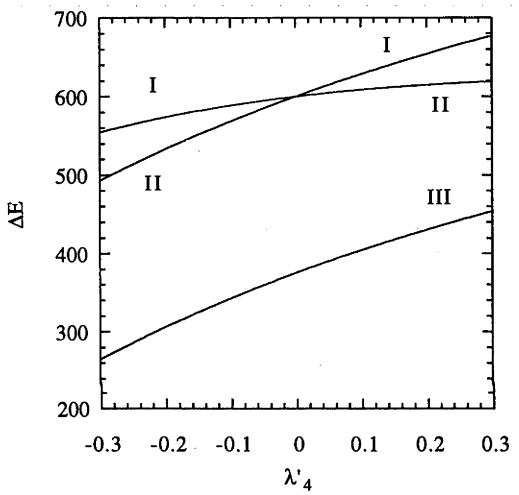

Figure 3.3: The effect of the $\hat{n}_{p1}\hat{n}_{p2}$ symmetry breaking term with strength parameter σ'_{12} on the excitation energy ΔE. I-III are as before.

CHAPTER 4

Summary and Conclusions

In this thesis, analytic $1/N$ expansion solutions for the vibron model of diatomic and linear triatomic molecules have been developed. The $1/N$ expansion method can be applied to an arbitrary vibron Hamiltonian, thus it generalizes the analytic formulation obtained in dynamical symmetry limits, providing a link between them. The results are used in a systematic study of symmetry breaking effects in energy levels and electric transitions among them. It is shown that the O(4) dynamical symmetry results can be improved by including symmetry breaking terms in the Hamiltonian. Symmetry breaking could offer a more economical and physical description of spectroscopic data compared to the symmetry preserving approach, and should be considered in detailed studies in future. Parameter systematics presented here would be very useful in numerical investigations of the vibron model as they restrict the allowed ranges of parameters, reducing the fitting procedure to one of a fine tuning.

A unique feature of the U(4) algebra is that it provides the simplest, non-trivial SGA that can be solved exactly using the $1/N$ expansion method. This is possible because diatomic molecules possess axial symmetry in the intrinsic frame, which simplifies the formalism and allows evaluation of the projection integrals in closed form. (In the IBM, except in the SU(3) limit, axial symmetry is realized only approximately, hence the solutions are not exact at higher orders.) In this sense, the $1/N$ expansion in the vibron model could play a similar role to the Lipkin model [28], which has been widely used in testing various many-body techniques. Because the vibron model is formulated in three dimensions instead of one, it can also be used in checking accuracy of approximate angular momentum projection methods such as cranking. We note that the solutions obtained for the ground-band energies and transitions are exact, but there are slight discrepancies in the vibrational bands. Namely, the ansatz (2.29), generalized from the O(4) wavefunctions, reproduces the numerical diagonalization results for the energies and inband transitions, but leads

to small discrepancies in spin-dependent terms of interband transitions. While this has no practical consequences, it suggests that the vibrational bands are likely to have more complicated forms in the intrinsic frame than those given in Eq. (2.29).

Extension of the diatomic results to linear triatomic molecules is straightforward but cumbersome due to the length of the formulas. The spectroscopic data in triatomic molecules focus on vibrational overtones more than the rotational bands built on top of them. Therefore, a systematic investigation of the moment of inertia in triatomic molecules, similar to the diatomic case, could not be given.

The simplicity of the vibron model also allows one to go beyond the usual boundaries of the IBM, and explore, for example, the effects many-body terms in the Hamiltonian and transition operators, as well as multi-phonon bands. Since the formalism in both models is very similar, one could extract lessons for the IBM from the present results. The variation of MOI with bands provides a relevant example. In both collective nuclei and molecules, the MOI of $K = 0$ bands gets larger with increasing phonon number. Reproducing this feature in the IBM has been an outstanding problem [29]. Inspection of Fig. 2.4 shows that the positive one-body term $\hat{n}_d$ could be the source of the problem, and an attractive two-body term $\hat{n}_d^2$ is needed to compensate for it and to make the MOI in the β band larger.

Finally, the results presented here form the basis for extensions of the vibron model to polyatomic molecules and reaction processes. A clear understanding of a single molecular bond in the vibron model is necessary before the $1/N$ expansion technique can be applied to more complex molecules. Since the $1/N$ expansion formalism provides simple wave functions for general Hamiltonians, it can also be used in electron scattering [30,31], and other molecular collision processes [32]. The work done in this direction using the dynamical symmetries can be generalized to arbitrary cases using the $1/N$ expansion.

APPENDIX A

O(4) Results

The O(4) limit of the vibron model has been solved exactly using group theoretical techniques [3,4]. Since it provides a valuable reference point in both formulation of the $1/N$ expansion and checking the accuracy of the analytical formulas, this appendix collects some of the relevant results. The O(4) Casimir operator and its expectation value in a state $|N, v, L\rangle$ are given by

$$\begin{aligned} \hat{C}_2(O(4)) &= \hat{D} \cdot \hat{D} + \hat{L} \cdot \hat{L}, \\ \langle N, v, L|\hat{C}_2(O(4))|N, v, L\rangle &= N(N+2) - 4(N+1)v + 4v^2. \end{aligned} \tag{A.1}$$

Thus the energy eigenvalues of the O(4) Hamiltonian

$$H(O(4)) = AC(O(4)) + BC(O(3), \tag{A.2}$$

are given by

$$\langle N, v, L|\hat{H}_{O4}|N, v, L\rangle = A\Big(N(N+2) - 4(N+1)v + 4v^2\Big) + B\bar{L}. \tag{A.3}$$

Explicit expressions for the O(4) wave functions, both in the coordinate space and the second quantized form, are available in literature [4]. A particularly useful recursion relation that allows construction of the vibrational bands from the ground band of is systems with lower boson number

$$|N, v, L\rangle = \mathcal{C}_{Nv}(s^\dagger s^\dagger - \vec{p}^\dagger \cdot \vec{p}^\dagger)^v |N - 2v, 0, L\rangle, \tag{A.4}$$

where $\mathcal{C}_{Nv}$ is a normalization factor.

$$\mathcal{C}_{Nv} = (-2)^{-v} \left[\frac{(N-2v+1)!}{v!(N-v+1)!}\right]^{1/2}. \tag{A.5}$$

Rewriting the ground band state as a projection from the condensate $|N-2v, 0, L\rangle \propto P^L_{00}|N-2v, 0\rangle$, and noting that the projection operator commutes with the scalar

operator $(s^\dagger s^\dagger - \vec{p}^\dagger \cdot \vec{p}^\dagger)$, it is clear that intrinsic states have the same form as in Eq. (A.4)

$$|N, v\rangle = C_{Nv}(s^\dagger s^\dagger - \vec{p}^\dagger \cdot \vec{p}^\dagger)^v |N - 2v, 0\rangle. \tag{A.6}$$

In terms of the intrinsic boson operators $b = (s + p_0)/\sqrt{2}$, $b' = (s - p_0)/\sqrt{2}$, the vibrational bands in (A.6) can be written as

$$|N, v\rangle = 2^v C_{Nv}[(N - 2v)!]^{-1/2} \left[b^\dagger b'^\dagger + p_1^\dagger p_{-1}^\dagger\right]^v (b^\dagger)^{N-2v}|0\rangle. \tag{A.7}$$

Matrix elements of various operators have been calculated in the O(4) limit [3,4]. Some that are used in checking the $1/N$ expansion results are

$$\langle N, v, L|\hat{n}_p|N, v, L\rangle = \frac{N-1}{2} + \frac{(N+2)\bar{L}}{2(N-2v)(N-2v+2)}. \tag{A.8}$$

$$\langle N, v, L+1|\hat{D}|N, v, L\rangle = [(L+1)(N-2v+L+2)(N-2v-L)]^{1/2}. \tag{A.9}$$

APPENDIX B

Evaluation of Normalization Integrals

The methods used in the evaluation of the normalization integrals exploit specific properties of single-boson SGA and neither can be generalized to multi-boson SGA, where Z^N in Eq. (2.21) is replaced by the product $Z_1^{N_1} Z_2^{N_2} \ldots$. What is needed in such cases is a simple ansatz for each Z^N, which can be improved in accuracy to any desired order in $1/N$. The Gaussian approximation used in the earlier papers [5], provides the germ for such an ansatz. We develop this approach here for the single-boson system and show, by comparing with the exact results obtained in [22], that it indeed provides a viable technique in the case of multi-boson SGA.

The basic Gaussian approximation involves substituting in (2.21)

$$[Z(\beta)]^N \simeq \exp[-aN\beta^2/4], \tag{B.1}$$

and evaluating instead the integral

$$I_0 = \int_0^\infty d\beta \sin\beta \, P_L(\beta) \exp[-aN\beta^2/4]. \tag{B.2}$$

In Eq. (B.1), the coefficients of the exponential follow from $Z(0) = 1$ and matching the second derivatives at $\beta = 0$. Using the technique described in Ref. [5], the integral (B.2) can be evaluated to arbitrary accuracy in $1/N$. It leads to the same form as in Eq. (2.27) but with different coefficients α_{nm}. The second and third layer results are listed below (the first layer coefficients remain the same, $\alpha_{nn} = 1$)

$$\alpha_{10} = 2/3, \quad \alpha_{21} = 2, \quad \alpha_{32} = 4, \quad \alpha_{43} = 20/3, \quad \alpha_{54} = 10, \quad \alpha_{65} = 14,$$

$$\alpha_{20} = 8/15, \quad \alpha_{31} = 12/5, \quad \alpha_{42} = 20/3, \quad \alpha_{53} = 44/3, \quad \alpha_{64} = 28. \tag{B.3}$$

Comparison of the Gaussian approximation results (B.3) with the exact ones (2.28) shows that the leading term in each power of $\bar{L}$ (i.e. the first layer) is correct but the higher order terms in $1/N$ deviate. Since the Gaussian approximation

matches the 1 and β^2 terms in the Taylor expansion of Z^N and the exponential (B.1) around $\beta = 0$, an improved approximation for Z^N should be of the form

$$[Z(\beta)]^N \simeq \exp[-aN\beta^2/4]\left(1 + c_4\beta^4 + c_6\beta^6 + c_8\beta^8 + \ldots\right). \tag{B.4}$$

The coefficients c_k in (B.4) can be obtained by Taylor expanding both sides of Eq. (B.4) and matching the powers of β^k. The Taylor expansion of an even function $f(\beta)$ around $\beta = 0$ is given by

$$f(\beta) = \sum_{k=\text{even}} f^{(k)}(0)\frac{\beta^k}{k!}, \tag{B.5}$$

where $f^{(k)}(0)$ denotes the k'th derivative of f at $\beta = 0$. For the ansatz (B.4), these derivatives can be easily generated using Mathematica [24]. For a general Z^N, they are a bit more involved. Therefore a list of the required derivatives as well as the method of derivation is given in Appendix C. Equating the respective derivatives of the ansatz in (B.4) and Z^N, Eq. (C.6), the following set of equations for c_k up to $k = 8$ is obtained

$$\begin{aligned}
&4!c_4 + \frac{3}{4}(aN)^2 = \frac{3}{4}N(N-1)a^2 + \frac{1}{8}N(3a_1 - 2a),\\
&6!c_6 - 180aNc_4 - \frac{15}{8}(aN)^3\\
&\quad = -\frac{15}{8}N(N-1)(N-2)a^3 - \frac{15}{16}N(N-1)(3a_1-2a)a - \frac{N}{16}(5a_2 - 10a_1 + 8a),\\
&8!c_8 - 10080aNc_6 + 1260(aN)^2c_4 + \frac{105}{16}(aN)^4\\
&\quad = \frac{105}{16}N(N-1)(N-2)(N-3)a^4 + \frac{210}{32}N(N-1)(N-2)(3a_1-2a)a^2\\
&\qquad + \frac{7}{64}N(N-1)\left[8(5a_2 - 10a_1 + 8a)a + 5(3a_1 - 2a)^2\right]\\
&\qquad + \frac{N}{128}(35a_3 - 140a_2 + 308a_1 - 272a),
\end{aligned} \tag{B.6}$$

where a_n is defined in Eq. (C.5). Note that for $c_k = 0$ (i.e. the Gaussian approximation), the leading power of N in each equation are matched but there are no $1/N$ correction terms on the left hand side, which illustrates the successes and failures of the Gaussian approximation. The ladder type of linear equations (B.6) for c_k can be easily solved to yield

$$\begin{aligned}
c_4 &= \frac{N}{2^3 4!}\left(3a_1 - 2a - 6a^2\right),\\
c_6 &= \frac{2N}{2^5 6!}\left[-5a_2 + 10a_1 - 8a + 15(3a_1 - 2a)a - 60a^3\right],\\
c_8 &= \frac{N}{2^7 8!}\Big\{35a_3 - 140a_2 + 308a_1 - 272a - 14\left[8(5a_2 - 10a_1 + 8a)a + 5(3a_1 - 2a)^2\right]\\
&\qquad +1680(3a_1 - 2a)a^2 - 5040a^4 + 70N\left(3a_1 - 2a - 6a^2\right)^2\Big\}.
\end{aligned} \tag{B.7}$$

The integrals that result from the improved Gaussian approximation (B.4) have extra factors of β^k. These can be obtained from the original integral I_0 by noticing that each derivative of Eq. (B.2) with respect to N brings in a factor of $-a\beta^2/4$ to the integrand. Thus, the integral improved to order β^m, denoted by I_m, can be written in terms of I_0 as

$$I_m = \left[1 + \sum_{k=2}^{m/2} c_{2k} \left(\frac{-4}{a}\right)^k \frac{\partial^k}{\partial N^k}\right] I_0. \tag{B.8}$$

It is instructive to examine the N dependence of each correction term in Eq. (B.8), and compare the results of a particular I_m with the exact ones given in Eq. (2.28). For I_4, the correction is of order $1/N$. Thus the first layer coefficients α_{nn} remain intact but the higher layers in I_0 are modified. In particular, the second layer coefficients α_{nn-1} become

$$\{\alpha_{nn-1}\}_4 = \{\alpha_{nn-1}\}_0 - \frac{n^2(n+1)}{12a}(3a_1 - 2a - 6a^2)\{\alpha_{n-1n-1}\}_0. \tag{B.9}$$

where the subscripts on $\{\alpha_{nm}\}$'s refer to the integral I_m it belongs. Substituting the coefficients $\{\alpha_{nm}\}_0$ (B.3) in Eq. (B.9), it can easily be checked that $\{\alpha_{nn-1}\}_4$ reproduce the exact results given in (2.28). Thus, I_4 is sufficient to obtain the second layer coefficients correctly (i.e. it provides the $1/N$ correction to the Gaussian approximation).

As stressed in Ref. [22], to describe the high-spin states in nuclear or molecular spectra, one needs the third layer coefficients in the norm integral. Inspection of Eqs. (B.7) and (B.8) shows that both the c_6 and c_8 terms contribute to the order $1/N^2$. Therefore one has to consider the integral I_8 for this purpose (contribution of c_{10} is of order $1/N^3$). Compared to I_4, the coefficients of the first and second layers in I_8 remain the same, and those of the third layer are given by

$$\begin{aligned}\{\alpha_{nn-2}\}_8 = \{\alpha_{nn-2}\}_0 &- \frac{n^2(n+1)}{12a}(3a_1 - 2a - 6a^2)\{\alpha_{n-1n-2}\}_0 \\ &+ \frac{(n-1)^2n^2(n+1)}{180a}\Big\{\left[-5a_2 + 10a_1 - 8a + 15(3a_1 - 2a)a - 60a^3\right] \\ &+ \frac{5(n+2)}{8a}\left(3a_1 - 2a - 6a^2\right)^2\Big\}\{\alpha_{n-2n-2}\}_0.\end{aligned} \tag{B.10}$$

Again substituting $\{\alpha_{nm}\}_0$ from (B.3) in Eq. (B.10), one can directly verify that $\{\alpha_{nn-2}\}_8$ reproduces the exact results given in (2.28). Calculations for higher layers become increasingly laborious. Nevertheless, the method is well adapted to computer algebra, and if needed, the higher layers can be easily generated using Mathematica.

APPENDIX C

Derivatives of Z^N

The derivatives of $f = Z^N$, $f^{(k)}$, can be written in terms of the derivatives of Z as

$$\begin{aligned}
f^{(1)} &= NZ^{N-1}Z^{(1)}, \\
f^{(2)} &= N(N-1)Z^{N-2}(Z^{(1)})^2 + NZ^{N-1}Z^{(2)}, \\
f^{(3)} &= N(N-1)(N-2)Z^{N-3}(Z^{(1)})^3 + 3N(N-1)Z^{N-2}Z^{(1)}Z^{(2)} + NZ^{N-1}Z^{(3)}, \\
f^{(4)} &= N(N-1)(N-2)(N-3)Z^{N-4}(Z^{(1)})^4 + 6N(N-1)(N-2)Z^{N-3} \\
&\quad \times (Z^{(1)})^2 Z^{(2)} + N(N-1)Z^{N-2}\left(3(Z^{(2)})^2 + 4Z^{(1)}Z^{(3)}\right) + NZ^{N-1}Z^{(4)}. \qquad \text{(C.1)}
\end{aligned}$$

The higher derivatives of Z^N can be easily generated using Mathematica, therefore, only the first few derivatives needed for discussion are given here. From Eq. (2.20), the derivatives of Z are given by

$$Z^{(k)} = \sum_l x_l^2 \, P_l^{(k)}(\beta), \qquad \text{(C.2)}$$

which require the derivatives of the Legendre functions with respect to β. These can be generated recursively using the chain rule for $z = \cos\beta$ together with the well known formula

$$\left.\frac{d^k P_l(\cos\beta)}{d(\cos\beta)^k}\right|_{\beta=0} = \frac{(-1)^k}{2^k k!}(l+1)_k(-l)_k, \qquad \text{(C.3)}$$

where $(l)_k = l(l+1)\cdots(l+k-1)$. The odd derivatives of P_l vanish at $\beta = 0$ due to the common $\sin\beta$ factor, and the even ones are given by

$$\begin{aligned}
P_l^{(2)} &= -\frac{1}{2}\bar{l}, \\
P_l^{(4)} &= \frac{1}{8}(3\bar{l}^2 - 2), \\
P_l^{(6)} &= -\frac{1}{16}(5\bar{l}^3 - 10\bar{l}^2 + 8\bar{l}), \\
P_l^{(8)} &= \frac{1}{128}(35\bar{l}^4 - 140\bar{l}^3 + 308\bar{l}^2 - 272\bar{l}). \qquad \text{(C.4)}
\end{aligned}$$

Since $Z^{(k)}$ are proportional to $P_l^{(k)}$, the odd derivatives of Z also vanish at $\beta = 0$. Introducing

$$a_n = \sum_l \bar{l}\, n + 1 x_l^2, \tag{C.5}$$

the even derivatives of Z are obtained from Eq. (C.4) by substituting $\bar{l}^{n+1} \to a_n$. This follows from using the definition of a_n (C.5) in Eqs. (C.2) and (C.4).

Going back to Eq. (C.1), after substituting $Z = 1$ and the values of $Z^{(k)}$ obtained above, we see that the odd derivatives of Z^N contain only the odd derivatives of Z, and hence they vanish at $\beta = 0$. Most of the terms in the even derivatives of Z^N also vanish for the same reason, and the remaining terms yield

$$\begin{aligned}
f^{(2)} &= -\frac{1}{2}Na, \\
f^{(4)} &= \frac{3}{4}N(N-1)a^2 + \frac{1}{8}N(3a_1 - 2a), \\
f^{(6)} &= -\frac{15}{8}N(N-1)(N-2)a^3 - \frac{15}{16}N(N-1)(3a_1 - 2a)a - \frac{N}{16}(5a_2 - 10a_1 + 8a), \\
f^{(8)} &= \frac{105}{16}N(N-1)(N-2)(N-3)a^4 + \frac{210}{32}N(N-1)(N-2)(3a_1 - 2a)a^2 \\
&\quad + \frac{7}{64}N(N-1)\Big[8(5a_2 - 10a_1 + 8a)a + 5(3a_1 - 2a)^2\Big] \\
&\quad + \frac{N}{128}(35a_3 - 140a_2 + 308a_1 - 272a).
\end{aligned} \tag{C.6}$$

APPENDIX D

Angular Momentum Sums

In evaluating matrix elements, one often needs to couple the d-functions with Clebsch-Gordan coefficients using

$$d^L_{mn} d^{L'}_{m'n'} = \sum_J \langle LmL'm'|J\mu\rangle \langle LnL'n'|J\mu'\rangle d^J_{\mu\mu'}. \tag{D.1}$$

After the angular integration, Eq. (D.1) leads to angular momentum sums with the d-function replaced by powers of $\bar{J}$. These sums can be evaluated using the techniques described in Appendix B of Ref. [5]. The results for the case $m = m' = n = n' = 0$ are encountered most in this paper, and these are given here as an example

$$S_n = \sum_J \langle L0L'0|J0\rangle^2 \bar{J}^n. \tag{D.2}$$

The first few of the sums are given by

$$\begin{aligned}
&S_0 = 1, \quad S_1 = \bar{L} + \bar{L}', \quad S_2 = \bar{L}^2 + 4\bar{L}\bar{L}' + \bar{L}'^2, \\
&S_3 = \bar{L}^3 + \bar{L}\bar{L}'(9\bar{L} + 9\bar{L}' - 4) + \bar{L}'^3, \\
&S_4 = \bar{L}^4 + 4\bar{L}\bar{L}'(4\bar{L}^2 + 9\bar{L}\bar{L}' + 4\bar{L}'^2 - 5(\bar{L} + \bar{L}') + 4) + \bar{L}'^4.
\end{aligned} \tag{D.3}$$

APPENDIX E

Operator Derivatives

This appendix contains the operator derivatives that are used in the calculations carried out in the thesis. The first section contains those relevant to calculations dealing with diatomic molecules. The second section gives the derivatives used in for the linear triatomic molecular calculations.

E.1 Single boson operators

The derivatives of the simplest operator,$\hat{n}_p$, are given below. These derivatives also may be used, with appropriate factors, for the one-body derivatives of higher powers of this operator.

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b_R}\hat{n}_p\right) = x_1^2 d_{00}^1 \tag{E.1}$$

$$\left(\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial b_R}\hat{n}_p\right) = x_1 d_{\pm 10}^1 \tag{E.2}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{n}_p\right) = x_1^2 d_{0\pm 1}^1 \tag{E.3}$$

$$\left(\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial p_{\mp 1\,R}}\hat{n}_p\right) = x_1^2 d_{\pm 1\mp 1}^1 \tag{E.4}$$

$$\left(\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{n}_p\right) = x_1^2 d_{\pm 1\pm 1}^1 \tag{E.5}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b_R}\hat{n}_p\right) = x_1'^2 d_{00}^1 \tag{E.6}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'_R}\hat{n}_p\right) = x_1 x_1' d_{00}^1 \tag{E.7}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b'_R}\hat{n}_p\right) = x_1 x_1' d_{00}^1 \tag{E.8}$$

$$\left(\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial b'_R}\hat{n}_p\right) = x'_1 d^1_{\pm 10} \tag{E.9}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{n}_p\right) = x'^2_1 d^1_{0\pm 1} \tag{E.10}$$

As shown in Eq. (2.58) the $\hat{n}_p^2$ operator can be written in a normal ordered form where the corresponding one-body interaction is exactly the operator $\hat{n}_p$. Thus the one-body derivatives of this two-body operator are the same as the derivatives of the one-body operator shown above. Therefore, only the two-body derivatives are presented.

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial^2}{\partial b_R^2}\hat{n}_p^2\right) = \frac{4}{3}x_1^4\left(1+2d^2_{00}\right) \tag{E.11}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b_R^2}\hat{n}_p^2\right) = \frac{4}{\sqrt{3}}x_1^3 d^2_{\pm 10} \tag{E.12}$$

$$\left(\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial^2}{\partial b_R^2}\hat{n}_p^2\right) = \frac{4}{3}x_1^2\left(d^2_{00}-1\right) \tag{E.13}$$

$$\left(\frac{\partial^2}{\partial p^{\dagger 2}_{\pm 1}}\frac{\partial^2}{\partial b_R^2}\hat{n}_p^2\right) = 4\sqrt{\frac{2}{3}}x_1^2 d^2_{\pm 20} \tag{E.14}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{n}_p^2\right) = \frac{4}{\sqrt{3}}x_1^3 d^2_{0\pm 1} \tag{E.15}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{n}_p^2\right) = 2x_1^2 d^2_{\pm 1\pm 1} \tag{E.16}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial p_{\mp 1\,R}}\frac{\partial}{\partial b_R}\hat{n}_p^2\right) = 2x_1^2 d^2_{\pm 1\mp 1} \tag{E.17}$$

$$\left(\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{n}_p^2\right) = \frac{2}{\sqrt{3}}x_1 d^2_{0\pm 1} \tag{E.18}$$

$$\left(\frac{\partial^2}{\partial p^{\dagger 2}_1}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{n}_p^2\right) = \frac{4}{\sqrt{2}}x_1 d^2_{2\pm 1} \tag{E.19}$$

$$\left(\frac{\partial^2}{\partial p^{\dagger 2}_{-1}}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{n}_p^2\right) = \frac{4}{\sqrt{2}}x_1 d^2_{-2\pm 1} \tag{E.20}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{n}_p^2\right) = \frac{4}{3}x_1^2\left(d^2_{00}-1\right) \tag{E.21}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{n}_p^2\right) = \frac{2}{\sqrt{3}}x_1 d^2_{\pm 10} \tag{E.22}$$

$$\left(\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{n}_p^2\right) = \frac{2}{3}\left(2+d^2_{00}\right) \tag{E.23}$$

$$\left(\frac{\partial^2}{\partial p^{\dagger 2}_{\pm 1}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{n}_p^2\right) = \frac{4}{\sqrt{6}}d^2_{\pm 20} \tag{E.24}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial^2}{\partial p^2_{\pm 1\,R}}\hat{n}_p^2\right) = 4\sqrt{\frac{2}{3}}x_1^2 d^2_{0\pm 2} \tag{E.25}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_1^\dagger}\frac{\partial^2}{\partial p^2_{\pm 1\,R}}\hat{n}_p^2\right) = \frac{4}{\sqrt{2}}x_1 d^2_{1\pm 2} \tag{E.26}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{-1}^\dagger}\frac{\partial^2}{\partial p^2_{\pm 1\,R}}\hat{n}_p^2\right) = \frac{4}{\sqrt{2}}x_1 d^2_{-1\pm 2} \tag{E.27}$$

$$\left(\frac{\partial}{\partial p_1^\dagger}\frac{\partial}{\partial p_{-1}^\dagger}\frac{\partial^2}{\partial p^2_{\pm 1\,R}}\hat{n}_p^2\right) = \frac{4}{\sqrt{6}}d^2_{0\pm 2} \tag{E.28}$$

$$\left(\frac{\partial^2}{\partial p_1^{\dagger 2}}\frac{\partial^2}{\partial p^2_{\pm 1\,R}}\hat{n}_p^2\right) = 4d^2_{2\pm 2} \tag{E.29}$$

$$\left(\frac{\partial^2}{\partial p_{-1}^{\dagger 2}}\frac{\partial^2}{\partial p^2_{\pm 1\,R}}\hat{n}_p^2\right) = 4d^2_{-2\pm 2} \tag{E.30}$$

The dipole operator $\hat{D}\cdot\hat{D}$, has also been written in normal ordered form (2.63). However, the one-body elements of this form contain the operator $\hat{n}_s$. Therefore the single derivatives of $\hat{D}\cdot\hat{D}$ are given here for convenience, followed by the two-body derivatives.

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = 3x_0^2 + x_1^2 d^1_{00} \tag{E.31}$$

$$\left(\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = x_1 d^1_{\pm 10} \tag{E.32}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{D}\cdot\hat{D}\right) = x_1 d^1_{0\pm 1} \tag{E.33}$$

$$\left(\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial p_{\mp 1\,R}}\hat{D}\cdot\hat{D}\right) = d^1_{\pm 1\mp 1} \tag{E.34}$$

$$\left(\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{D}\cdot\hat{D}\right) = d^1_{\pm 1\pm 1} \tag{E.35}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b'_R}\hat{D}\cdot\hat{D}\right) = 3x_0'^2 + x_1'^2 d^1_{00} \tag{E.36}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'_R}\hat{D}\cdot\hat{D}\right) = 3x_0 x_0' + x_1 x_1' d^1_{00} \tag{E.37}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = 3x_0 x_0' + x_1 x_1' d^1_{00} \tag{E.38}$$

$$\left(\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial b'_R}\hat{D}\cdot\hat{D}\right) = x_1' d^1_{\pm 10} \tag{E.39}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{D}\cdot\hat{D}\right) = x_1' d^1_{0\pm 1} \tag{E.40}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial^2}{\partial b_R^2}\hat{D}\cdot\hat{D}\right) = 8x_0^2x_1^2\left(1+d_{00}^1\right) \quad \text{(E.41)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = 4x_0x_1\left(x_1x_0'+x_0x_1'\right)\left(1+d_{00}^1\right) \quad \text{(E.42)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b_R'}\hat{D}\cdot\hat{D}\right) = 4x_0x_1\left(x_1x_0'+x_0x_1'\right)\left(1+d_{00}^1\right) \quad \text{(E.43)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b_R'}\hat{D}\cdot\hat{D}\right) = 8x_0x_1x_0'x_1' + 2\left(x_0x_1'+x_1x_0'\right)^2 d_{00}^1 \quad \text{(E.44)}$$

$$\left(\frac{\partial^2}{\partial b'^{\dagger 2}}\frac{\partial^2}{\partial b_R^2}\hat{D}\cdot\hat{D}\right) = 4(x_0^2x_1'^2 + x_0'^2x_1^2 + 2x_0x_0'x_1x_1'd_{00}^1) \quad \text{(E.45)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial^2}{\partial b_R'^2}\hat{D}\cdot\hat{D}\right) = 4(x_0^2x_1'^2 + x_0'^2x_1^2 + 2x_0x_0'x_1x_1'd_{00}^1) \quad \text{(E.46)}$$

$$\left(\frac{\partial^2}{\partial b'^{\dagger 2}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b'^\dagger}\hat{D}\cdot\hat{D}\right) = 4x_0'x_1'(x_0'x_1+x_0x_1')(1+d_{00}^1) \quad \text{(E.47)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial^2}{\partial b'^{\dagger 2}}\hat{D}\cdot\hat{D}\right) = 4x_0'x_1'(x_0'x_1+x_0x_1')(1+d_{00}^1) \quad \text{(E.48)}$$

$$\left(\frac{\partial^2}{\partial b'^{\dagger 2}}\frac{\partial^2}{\partial b_R'^2}\hat{D}\cdot\hat{D}\right) = 8x_0'^2x_1'^2(1+d_{00}^1) \quad \text{(E.49)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial^2}{\partial b_R^2}\hat{D}\cdot\hat{D}\right) = 4x_0^2x_1d_{\pm 10}^1 \quad \text{(E.50)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b_R'}\hat{D}\cdot\hat{D}\right) = 2\left(x_0^2x_1'+x_0x_1x_0'\right)d_{\pm 10}^1 \quad \text{(E.51)}$$

$$\left(\frac{\partial}{\partial p_1^\dagger}\frac{\partial}{\partial p_{-1}^\dagger}\frac{\partial^2}{\partial b_R^2}\hat{D}\cdot\hat{D}\right) = -4x_0^2 \quad \text{(E.52)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = 4x_0^2x_1d_{0\pm 1}^1 \quad \text{(E.53)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = 2\left(x_0^2x_1'+x_0x_1x_0'\right)d_{0\pm 1}^1 \quad \text{(E.54)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = 2x_0^2d_{\pm 1\pm 1}^1 \quad \text{(E.55)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{\pm 1}^\dagger}\frac{\partial}{\partial p_{\mp 1\,R}}\frac{\partial}{\partial b_R}\hat{D}\cdot\hat{D}\right) = 2x_0^2d_{\pm 1\mp 1}^1 \quad \text{(E.56)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{D}\cdot\hat{D}\right) = -4x_0^2 \quad \text{(E.57)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{D}\cdot\hat{D}\right) = 2x_0(x_0'x_1+x_0x_1')d_{0\pm 1}^1 \quad \text{(E.58)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b'_R}\hat{D}\cdot\hat{D}\right) = 2x_0(x'_0x_1+x_0x'_1)d^1_{\pm 10} \quad \text{(E.59)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{D}\cdot\hat{D}\right) = -4x_0x'_0 \quad \text{(E.60)}$$

$$\left(\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b'_R}\hat{D}\cdot\hat{D}\right) = -4x_0x'_0 \quad \text{(E.61)}$$

$$\left(\frac{\partial^2}{\partial b'^{\dagger 2}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{D}\cdot\hat{D}\right) = 4x_0x'_0x_1d^1_{0\pm 1} \quad \text{(E.62)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b'^2_R}\hat{D}\cdot\hat{D}\right) = 4x_0x'_0x_1d^1_{\pm 10} \quad \text{(E.63)}$$

$$\left(\frac{\partial^2}{\partial b'^{\dagger 2}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{D}\cdot\hat{D}\right) = -4x'^2_0 \quad \text{(E.64)}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\hat{D}\cdot\hat{D}\right) = 2x'_0(x'_0x_1+x_0x'_1)d^1_{\pm 10} \quad \text{(E.65)}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p_{\pm 1\,R}}\frac{\partial}{\partial b'^\dagger}\hat{D}\cdot\hat{D}\right) = 2x'_0(x'_0x_1+x_0x'_1)d^1_{0\pm 1} \quad \text{(E.66)}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial b'_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{D}\cdot\hat{D}\right) = 2x'^2_0d^1_{\pm 1\pm 1} \quad \text{(E.67)}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial b'_R}\frac{\partial}{\partial p_{\mp 1\,R}}\hat{D}\cdot\hat{D}\right) = 2x'^2_0d^1_{\pm 1\mp 1} \quad \text{(E.68)}$$

$$\left(\frac{\partial^2}{\partial b'^{\dagger 2}}\frac{\partial}{\partial b'_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{D}\cdot\hat{D}\right) = 4x'^2_0x'_1d^1_{0\pm 1} \quad \text{(E.69)}$$

$$\left(\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b'^2_R}\hat{D}\cdot\hat{D}\right) = 4x'^2_0x'_1d^1_{\pm 10} \quad \text{(E.70)}$$

Eq. (2.58) gives the normal ordered form of $\hat{n}^3_p$. It may be seen from this equation that the one-body derivatives of the operator are given by the derivatives of $\hat{n}_p$ with a factor of (-2), and the two-body derivatives are given by those of $\hat{n}^2_p$ with a factor of 3. The three-body derivatives are presented below.

$$\left(\frac{\partial^3}{\partial b^{\dagger 3}}\frac{\partial^3}{\partial b^3_R}\hat{n}^3_p\right) = \frac{36}{5}x^6_1(3d^1_{00}+d^3_{00}) \quad \text{(E.71)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial b'^\dagger}\frac{\partial^3}{\partial b^3_R}\hat{n}^3_p\right) = \frac{36}{5}x^5_1x'_1(3d^1_{00}+d^3_{00}) \quad \text{(E.72)}$$

$$\left(\frac{\partial^3}{\partial b^{\dagger 3}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial b'_R}\hat{n}^3_p\right) = \frac{36}{5}x^5_1x'_1(3d^1_{00}+d^3_{00}) \quad \text{(E.73)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^3}{\partial b^3_R}\hat{n}^3_p\right) = \frac{12}{5}x^5_1(3d^1_{\pm 10}+2\sqrt{6}d^3_{\pm 10}) \quad \text{(E.74)}$$

$$\left(\frac{\partial^3}{\partial b^{\dagger 3}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{n}^3_p\right) = \frac{12}{5}x^5_1(3d^1_{0\pm 1}+2\sqrt{6}d^3_{0\pm 1}) \quad \text{(E.75)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial b'_R}\hat{n}^3_p\right) = \frac{12}{5}x_1^4 x'_1(3d^1_{\pm 10} + 2\sqrt{6}d^3_{\pm 10}) \quad \text{(E.76)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial b'^\dagger}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{n}^3_p\right) = \frac{12}{5}x_1^4 x'_1(3d^1_{0\pm 1} + 2\sqrt{6}d^3_{0\pm 1}) \quad \text{(E.77)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{n}^3_p\right) = \frac{12}{5}x_1^4(d^1_{\pm 1\pm 1} + 4d^3_{\pm 1\pm 1}) \quad \text{(E.78)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial p_{\mp 1\,R}}\hat{n}^3_p\right) = \frac{12}{5}x_1^4(d^1_{\pm 1\mp 1} + 4d^3_{\pm 1\mp 1}) \quad \text{(E.79)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial^2}{\partial p^{\dagger 2}_{\pm 1}}\frac{\partial^3}{\partial b^3_R}\hat{n}^3_p\right) = 12\sqrt{\frac{6}{5}}x_1^4 d^3_{\pm 20} \quad \text{(E.80)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial p^\dagger_{\mp 1}}\frac{\partial^3}{\partial b^3_R}n^3_p\right) = \frac{36}{5}x_1^4(d^3_{00} - d^1_{00}) \quad \text{(E.81)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial^2}{\partial p^{\dagger 2}_{\pm 1}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial b'_R}\hat{n}^3_p\right) = 12\sqrt{\frac{6}{5}}x_1^3 x'_1 d^3_{\pm 20} \quad \text{(E.82)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial p^\dagger_{\mp 1}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial b'_R}n^3_p\right) = \frac{36}{5}x_1^3 x'_1(d^3_{00} - d^1_{00}) \quad \text{(E.83)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial^2}{\partial p^{\dagger 2}_{\pm 1}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial p^\dagger_{\pm 1}}\hat{n}^3_p\right) = \frac{24}{\sqrt{5}}x_1^3 d^3_{\pm 2\pm 1} \quad \text{(E.84)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}n^3_p\right) = \frac{6}{5}x_1^2(2d^1_{00} + 3d^3_{00}) \quad \text{(E.85)}$$

The final derivatives to be considered in this section are those of $\hat{O}_3 = \hat{n}_p\hat{D}\cdot\hat{D} + \hat{D}\cdot\hat{D}\hat{n}_p$. The normal ordered form (2.73) shows that the single derivatives of this operator may be obtained from the derivatives of $\hat{n}_p$ with a factor of 2. However, it is necessary to give the remaining derivatives explicitly.

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial^2}{\partial b^2_R}\hat{O}_3\right) = 8x_1^2x_0^2(2 + 5d^1_{00}) + \frac{8}{3}x_1^4(1 + 2d^2_{00}) \quad \text{(E.86)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial^2}{\partial b^2_R}\hat{O}_3\right) = 4x_0x_1(x'_0x_1 + x_0x'_1)(2 + 5d^1_{00}) + \frac{8}{3}x_1^3x'_1(1 + 2d^2_{00}) \quad \text{(E.87)}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b'_R}\hat{O}_3\right) = 4x_0x_1(x'_0x_1 + x_0x'_1)(2 + 5d^1_{00}) + \frac{8}{3}x_1^3x'_1(1 + 2d^2_{00}) \quad \text{(E.88)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial b'^\dagger}\frac{\partial}{\partial b_R}\frac{\partial}{\partial b'_R}\hat{O}_3\right) = 12x_0x'_0x_1x'_1 + 10(x_0^2x_1'^2 + 2x_0x'_0x_1x'_1 + x_0'^2x_1^2)d^1_{00} + \frac{8}{3}x_1^2x_1'^2(1 + 2d^2_{00}) \quad \text{(E.89)}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b^2_R}\hat{O}_3\right) = 20x_0^2x_1d^1_{\pm 10} + \frac{8}{\sqrt{3}}x_1^3d^2_{\pm 10} \tag{E.90}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial^2}{\partial p^{\dagger 2}_{\pm 1}}\hat{O}_3\right) = 20x_0^2x_1d^1_{0\pm 1} + \frac{8}{\sqrt{3}}x_1^3d^2_{0\pm 1} \tag{E.91}$$

$$\left(\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial^2}{\partial b^{\dagger 2}}\hat{O}_3\right) = -\frac{8}{3}(3x_0^2 + x_1^2 + x_1^2d^2_{00}) \tag{E.92}$$

$$\left(\frac{\partial^2}{\partial p^{\dagger 2}_{\pm 1}}\frac{\partial^2}{\partial b^{\dagger 2}}\hat{O}_3\right) = 8\sqrt{\frac{2}{3}}x_1^2d^2_{\pm 20} \tag{E.93}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{O}_3\right) = -\frac{8}{3}(3x_0^2 + x_1^2 + x_1^2d^2_{00}) \tag{E.94}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{O}_3\right) = 10x_0^2d^1_{\pm 1\pm 1} + 4x_1^2d^2_{\pm 1\pm 1} \tag{E.95}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{\mp 1\,R}}\hat{O}_3\right) = 10x_0^2d^1_{\pm 1\mp 1} + 4x_1^2d^2_{\pm 1\mp 1} \tag{E.96}$$

$$\left(\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{O}_3\right) = \frac{4}{\sqrt{3}}x_1d^2_{0\pm 1} \tag{E.97}$$

$$\left(\frac{\partial}{\partial b^\dagger}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{O}_3\right) = \frac{4}{\sqrt{3}}x_1d^2_{\pm 10} \tag{E.98}$$

$$\left(\frac{\partial}{\partial p^\dagger_1}\frac{\partial}{\partial p^\dagger_{-1}}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{O}_3\right) = \frac{4}{3}(2 + d^2_{00}) \tag{E.99}$$

$$\left(\frac{\partial^3}{\partial b^{\dagger 3}}\frac{\partial^3}{\partial b^3_R}\hat{O}_3\right) = 48x_0^2x_1^4(1 + 3d^1_{00} + 2d^2_{00}) \tag{E.100}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial b'^\dagger}\frac{\partial^3}{\partial b^3_R}\hat{O}_3\right) = 16x_0x_1^3(x'_0x_1 + 2x_0x'_1)(1 + 3d^1_{00} + 2d^2_{00}) \tag{E.101}$$

$$\left(\frac{\partial^3}{\partial b^{\dagger 3}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial b'_R}\hat{O}_3\right) = 16x_0x_1^3(x'_0x_1 + 2x_0x'_1)(1 + 3d^1_{00} + 2d^2_{00}) \tag{E.102}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial b'^\dagger}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial b'_R}\hat{O}_3\right) = \frac{16}{3}x_1^2(x'^2_0x_1^2 + 4x_0x'_0x_1x'_1 + 4x_0^2x'^2_1)(1+2d^2_{00}) + 48x_1^2x'_1(2x_0x'_0x_1x'_1 + x_0^2x'^2_1)d^1_{00} \tag{E.103}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^3}{\partial b^3_R}\hat{O}_3\right) = 16x_0^2x_1^3(3d^1_{\pm 10} + 2\sqrt{3}d^2_{\pm 10}) \tag{E.104}$$

$$\left(\frac{\partial^3}{\partial b^{\dagger 3}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{O}_3\right) = 16x_0^2x_1^3(3d^1_{0\pm 1} + 2\sqrt{3}d^2_{0\pm 1}) \tag{E.105}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p^\dagger_{\pm 1}}\frac{\partial^2}{\partial b^2_R}\frac{\partial}{\partial b'^\dagger}\hat{O}_3\right) = \frac{16}{3}x_0x_1^2(x'_0x_1 + 2x_0x'_1)(3d^1_{\pm 10} + 2\sqrt{3}d^2_{\pm 10}) \tag{E.106}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial b'^{\dagger}}\frac{\partial^2}{\partial b_R^2}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{O}_3\right) = \frac{16}{3}x_0x_1^2(x_0'x_1+2x_0x_1')(3d_{0\pm 1}^1+2\sqrt{3}d_{0\pm 1}^2) \tag{E.107}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{\pm 1}^{\dagger}}\frac{\partial^2}{\partial b_R^2}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{O}_3\right) = 16x_0^2x_1^2(d_{\pm 1\pm 1}^1+2d_{\pm 1\pm 1}^2) \tag{E.108}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{\pm 1}^{\dagger}}\frac{\partial^2}{\partial b_R^2}\frac{\partial}{\partial p_{\mp 1\,R}}\hat{O}_3\right) = 16x_0^2x_1^2(d_{\pm 1\mp 1}^1+2d_{\pm 1\mp 1}^2) \tag{E.109}$$

$$\left(\frac{\partial}{\partial b^{\dagger}}\frac{\partial}{\partial p_1^{\dagger}}\frac{\partial}{\partial p_{-1}^{\dagger}}\frac{\partial^3}{\partial b_R^3}\hat{O}_3\right) = -8x_0^2x_1^2(2+3d_{00}^1-2d_{00}^2) \tag{E.110}$$

$$\left(\frac{\partial^3}{\partial b^{\dagger 3}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{O}_3\right) = -8x_0^2x_1^2(2+3d_{00}^1-2d_{00}^2) \tag{E.111}$$

$$\left(\frac{\partial}{\partial b^{\dagger}}\frac{\partial}{\partial p_1^{\dagger}}\frac{\partial}{\partial p_{-1}^{\dagger}}\frac{\partial^2}{\partial b_R^2}\frac{\partial}{\partial b'^{\dagger}}\hat{O}_3\right) = -\frac{8}{3}x_0x_1(2x_0'x_1+2x_0x_1'+3(2x_0'x_1 + x_0x_1')d_{00}^1-2(x_0'x_1+2x_0x_1')d_{00}^2) \tag{E.112}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial b'^{\dagger}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{O}_3\right) = -\frac{8}{3}x_0x_1(2x_0'x_1+2x_0x_1'+3(2x_0'x_1 + x_0x_1')d_{00}^1-2(x_0'x_1+2x_0x_1')d_{00}^2) \tag{E.113}$$

$$\left(\frac{\partial}{\partial b^{\dagger}}\frac{\partial}{\partial p_1^{\dagger}}\frac{\partial}{\partial p_{-1}^{\dagger}}\frac{\partial^2}{\partial b_R^2}\frac{\partial}{\partial p_{\pm 1\,R}}\hat{O}_3\right) = -\frac{8}{3}x_0^2x_1(3d_{0\pm 1}^1-2\sqrt{3}d_{0\pm 1}^2) \tag{E.114}$$

$$\left(\frac{\partial^2}{\partial b^{\dagger 2}}\frac{\partial}{\partial p_{\pm 1}^{\dagger}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{O}_3\right) = -\frac{8}{3}x_0^2x_1(3d_{\pm 10}^1-2\sqrt{3}d_{\pm 1}^2 0) \tag{E.115}$$

$$\left(\frac{\partial}{\partial b^{\dagger}}\frac{\partial}{\partial p_1^{\dagger}}\frac{\partial}{\partial p_{-1}^{\dagger}}\frac{\partial}{\partial b_R}\frac{\partial}{\partial p_{1\,R}}\frac{\partial}{\partial p_{-1\,R}}\hat{O}_3\right) = \frac{8}{3}x_0^2(2+d_{00}^2) \tag{E.116}$$

E.2 Two boson results

This section contains the derivatives used in the linear triatomic spectrum calculations.

$$\left(\frac{\partial}{\partial b_1^{\dagger}}\frac{\partial}{\partial b_2^{\dagger}}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{3}x_{1,1}^2x_{2,1}^2(1+2d_{00}^2) \tag{E.117}$$

$$\left(\frac{\partial}{\partial b_1'^{\dagger}}\frac{\partial}{\partial b_2^{\dagger}}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{3}x_{1,1}x_{1,1}'x_{2,1}^2(1+2d_{00}^2) \tag{E.118}$$

$$\left(\frac{\partial}{\partial b_1^{\dagger}}\frac{\partial}{\partial b_2^{\dagger}}\frac{\partial}{\partial b_{1\,R}'}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{3}x_{1,1}x_{1,1}'x_{2,1}^2(1+2d_{00}^2) \tag{E.119}$$

$$\left(\frac{\partial}{\partial b_1'^{\dagger}}\frac{\partial}{\partial b_2^{\dagger}}\frac{\partial}{\partial b_{1\,R}'}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{3}x_{1,1}'^2x_{2,1}^2(1+2d_{00}^2) \tag{E.120}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}'}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{3}x_{1,1}x'_{1,1}x_{2,1}x'_{2,1}(1+2d^2_{00}) \quad \text{(E.121)}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{3}x_{1,1}x'_{1,1}x_{2,1}x'_{2,1}(1+2d^2_{00}) \quad \text{(E.122)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{\sqrt{3}}x_{1,1}x^2_{2,1}(d^2_{10}+2d^2_{00}) \quad \text{(E.123)}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{\sqrt{3}}x_{1,1}x^2_{2,1}(d^2_{10}+2d^2_{00}) \quad \text{(E.124)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{2}x^2_{2,1}(d^1_{11}+d^2_{11}) \quad \text{(E.125)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b'_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{2}x_{1,1}x_{2,1}(-d^1_{11}+d^2_{11}) \quad \text{(E.126)}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{n}_1\cdot\hat{n}_2\right) = \frac{1}{2}x_{1,1}x_{2,1}(-d^1_{11}+d^2_{11}) \quad \text{(E.127)}$$

(E.128)

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = 2x_{1,0}x_{1,1}x_{2,0}x_{2,1}(1+d^1_{00}) \quad \text{(E.129)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = (x'_{1,0}x_{1,1}+x_{1,0}x'_{1,1})x_{2,0}x_{2,1}(1+d^1_{00}) \quad \text{(E.130)}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = (x'_{1,0}x_{1,1}+x_{1,0}x'_{1,1})x_{2,0}x_{2,1}(1+d^1_{00}) \quad \text{(E.131)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = 2x'_{1,0}x'_{1,1}x_{2,0}x_{2,1}(1+d^1_{00}) \quad \text{(E.132)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b'_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = x_{1,0}x'_{1,1}x'_{2,0}x_{2,1}+x'_{1,0}x_{1,1}x_{2,0}x'_{2,1}$$
$$+(x'_{1,0}x_{1,1}x'_{2,0}x_{2,1}+x_{1,0}x'_{1,1}x_{2,0}x'_{2,1})d^1_{00} \quad \text{(E.133)}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = x_{1,0}x'_{1,1}x'_{2,0}x_{2,1}+x'_{1,0}x_{1,1}x_{2,0}x'_{2,1} \quad \text{(E.134)}$$
$$+(x'_{1,0}x_{1,1}x'_{2,0}x_{2,1}+x_{1,0}x'_{1,1}x_{2,0}x'_{2,1})d^1_{00} \quad \text{(E.135)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = x_{1,0}x_{2,0}x_{2,1}d^1_{10} \quad \text{(E.136)}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = x_{1,0}x_{2,0}x_{2,1}d^1_{01} \quad \text{(E.137)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = 0 \quad \text{(E.138)}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b'_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = x_{1,0}x_{2,0}d^1_{11} \quad \text{(E.139)}$$

$$\left(\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{D}_1\cdot\hat{D}_2\right) = x_{1,0}x_{2,0}d_{11}^1 \tag{E.140}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = (x_{1,0}x_{2,1}-x_{1,1}x_{2,0})^2 d_{00}^1 \tag{E.141}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = (x_{1,1}x_{2,0}-x_{1,0}x_{2,1})(x'_{1,1}x_{2,0}-x'_{1,0}x_{2,1})d_{00}^1 \tag{E.142}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = (x_{1,1}x_{2,0}-x_{1,0}x_{2,1})(x'_{1,1}x_{2,0}-x'_{1,0}x_{2,1})d_{00}^1 \tag{E.143}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = (x'_{1,1}x_{2,0}-x'_{1,0}x_{2,1})^2 d_{00}^1 \tag{E.144}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b'_{2\,R}}\hat{M}_4'\right) = (x'_{1,1}x_{2,0}-x'_{1,0}x_{2,1})(x_{1,1}x'_{2,0}-x_{1,0}x'_{2,1})d_{00}^1 \tag{E.145}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = (x'_{1,1}x_{2,0}-x'_{1,0}x_{2,1})(x_{1,1}x'_{2,0}-x_{1,0}x'_{2,1})d_{00}^1 \tag{E.146}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = x_{2,0}(x_{1,1}x_{2,0}-x_{1,0}x_{2,1})d_{10}^1 \tag{E.147}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = x_{2,0}(x_{1,1}x_{2,0}-x_{1,0}x_{2,1})d_{01}^1 \tag{E.148}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = x_{2,0}^2 d_{11}^1 \tag{E.149}$$

$$\left(\frac{\partial}{\partial b_1'^\dagger}\frac{\partial}{\partial b_2^\dagger}\frac{\partial}{\partial b_{1\,R}}\frac{\partial}{\partial b'_{2\,R}}\hat{M}_4'\right) = -x_{1,0}x_{2,0}d_{11}^1 \tag{E.150}$$

$$\left(\frac{\partial}{\partial b_1^\dagger}\frac{\partial}{\partial b_2'^\dagger}\frac{\partial}{\partial b'_{1\,R}}\frac{\partial}{\partial b_{2\,R}}\hat{M}_4'\right) = -x_{1,0}x_{2,0}d_{11}^1 \tag{E.151}$$

APPENDIX F

Extended Triatomic Molecule Results

This appendix gives the excited band energies for triatomic molecules to second layer.

$$
\begin{aligned}
\langle \hat{n}^2_{p1} \rangle_L \;=\; & \frac{N_1^2 a_1^2}{4} + \frac{N_1}{4} a_1 (6 - 4a_1 + (4 - 3a_1)\cos(2\gamma)) \\
& - \frac{N_1^2}{2N}(2 - a_1) a_1^2 (2 + \cos(2\gamma)) \\
& - \frac{N_1^{3/2} N_2^{1/2}}{2N}(2 - a_1)(2 - a_2) a_1 r_1 r_2 \sin(2\gamma) \\
& + \frac{1}{4}(2 - 6a_1 + 3a_1^2)(1 + \cos(2\gamma)) \\
& - \frac{1}{8N} N_1 a_1 \Big(32 - 60a_1 + 23a_1^2 + 4a_2 - 3a_1 a_2 + 4(2 - a_1)(3 - 4a_1)\cos(2\gamma) \\
& \qquad + (4 - 3a_1)(a_1 - a_2)\cos(4\gamma) \Big) \\
& - \frac{1}{2N}(N_1 N_2)^{1/2}(2 - a_1)(1 - a_1)(2 - a_2) r_1 r_2 \sin(2\gamma) \\
& + \frac{1}{8^2} N_1^2 a_1^2 \Big(56(1 - 2a_1) - 6a_2(2 - a_2) + 39a_1^2 + 2a_1 a_2 \\
& \qquad + 2(8 - 24a_1 + 8a_2 + 11a_1^2 - 3a_2^2 - 2a_1 a_2)\cos(2\gamma) \\
& \qquad - (2 - a_1)(4 - 5a_1 + 2a_2)\cos(4\gamma) \Big) \\
& + \frac{1}{2N^2} N_1^{3/2} N_2^{1/2}(2 - a_1)(2 - a_2) a_1 r_1 r_2 (2 - 2a_1 + a_2 \\
& \qquad - (4 - 4a_1 + a_2)\cos(2\gamma))\sin(2\gamma) \\
& - \frac{1}{4N^2} N_1 N_2 (4 - 3a_1)(2 - a_2) a_1 a_2 \sin^2(2\gamma) \\
& + \frac{1}{4N^3} N_1^3 a_1^3 \Big(-2(2 - a_1)(1 - 9a_1) - 3a_1 a_2 \\
& \qquad + a_1(20 - 13a_1 + 3a_2)\cos(2\gamma) \\
& \qquad + (2 - a_1)^2 \cos(4\gamma) \Big)
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{2N^3}N_1^{5/2}N_2^{1/2}(2-a_1)(2-a_2)a_1^2r_1r_2(2-6a_1-3a_2)\\
&\qquad -(6-3a_1)\cos(2\gamma))\sin(2\gamma)\\
&+\frac{1}{4N^3}N_1^2N_2a_1^2a_2\Big(-4+2a_1+36a_2-12a_1a_2-9a_2^2\\
&\qquad +(16-8a_1-12a_2-3a_1a_2+9a_2^2)\cos(2\gamma)-3(2-a_1)(2-a_2)\cos(4\gamma)\Big)\\
&+\frac{1}{2N^3}(N_1N_2)^{3/2}(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(2+a_2-(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&-\frac{3}{N^4}N_1^4(2-a_1)a_1^5\cos^2(\gamma)-\frac{3}{N^4}(N_1N_2a_1)^2a_2^3(2-a_2)\sin^2(\gamma)\\
&+\frac{3}{N^4}N_1^3N_2a_1^2a_2\Big(a_1a_2-a_1-a_2+(a_1-a_2)\cos(2\gamma)\Big)\\
&-\frac{3}{N^4}N_1^{5/2}N_2^{1/2}\bar{a}^2N(2-a_1)(2-a_2)a_1^2r_1r_2\sin(2\gamma)\\
-&\frac{\bar{L}}{2N^2}\Big[N_1^2(2-a_1)a_1^2(2+\cos(2\gamma))\\
&+N_1^{3/2}N_2^{1/2}(2-a_1)(2-a_2)a_1r_1r_2\sin(2\gamma)\\
&+\frac{1}{8}N_1a_1\Big(32-60a_1+4a_2+23a_1^2-3a_1a_2+4(2-a_1)(3-4a_1)\cos(2\gamma)\\
&\qquad +(4-3a_1)(a_1-a_2)\cos(4\gamma)\Big)\\
&+\frac{1}{2}(N_1N_2)^{1/2}(2-a_1)(1-a_1)(2-a_2)r_1r_2\sin(2\gamma)\\
&+\frac{1}{4N}N_1^2a_1^2\Big(-34+91a_1+9a_2-39a_1^2-6a_2^2-2a_1a_2\\
&\qquad +(-8+41a_1-13a_2-22a_1^2+6a_2^2+4a_1a_2)\cos(2\gamma)\\
&\qquad +(2-a_1)(4-5a_1+2a_2)\cos(4\gamma)\Big)\\
&-\frac{1}{N}N_1^{3/2}N_2^{1/2}(2-a_1)(2-a_2)a_1r_1r_2\Big(1-2a_1-a_2-(4-4a_1+a_2)\cos(2\gamma)\Big)\\
&+\frac{1}{2N}N_1N_2a_1a_2(4-3a_1)(2-a_2)\sin^2(2\gamma)\\
&+\frac{3}{4N^2}N_1^3a_1^3\Big(3a_1(-12+6a_1+a_2)+(-4-18a_1+13a_1^2-3a_1a_2)\cos(2\gamma)\\
&\qquad -(2-a_1)^2\cos(4\gamma)\Big)\\
&-\frac{9}{2N^2}N_1^{5/2}N_2^{1/2}(2-a_1)(2-a_2)a_1^2r_1r_2\Big(2a_1+a_2+(2-a_1)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+\frac{3}{4N^2}N_1^2N_2a_1^2a_2\Big(-2a_1-34a_2+9a_2^2+12a_1a_2\\
&\qquad +(-12+8a_1+10a_2-9a_2^2+3a_1a_2)\cos(2\gamma)\\
&\qquad +3(2-a_1)(2-a_2)\cos(4\gamma)\Big)
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{3}{2N^2}(N_1N_2)^{3/2}(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(2+a_2-(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+\frac{12}{N^3}N_1^4(2-a_1)a_1^5\cos^2(\gamma)\\
&+\frac{12}{N^3}N_1^3N_2a_1^3a_2\Big(a_1+a_2-a_1a_2-(a_1-a_2)\cos(2\gamma)\Big)\\
&+\frac{12}{N^3}N_1^2N_2^2a_1^2a_2^3(2-a_2)\sin^2(\gamma)\\
&+\frac{12}{N^3}N_1^{5/2}N_2^{1/2}\bar{a}^2N(2-a_1)(2-a_2)a_1^2r_1r_2\sin(2\gamma)\Big]\\
+\frac{\bar{L}^2}{N^4}\Big[&\frac{1}{48}N_1^2a_1^2\Big(-80-122a_1+28a_2+87a_1^2+18a_2^2-12a_1a_2\\
&\quad+2(-24+2a_1-2a_2+15a_1^2-9a_2^2)\cos(2\gamma)\\
&\quad-3(2-a_1)(4-7a_1+4a_2)\cos(4\gamma)\Big)\\
&-\frac{1}{4}N_1^{3/2}N_1^{1/2}(2-a_1)a_1r_1r_2\Big((2-a_1)(2+a_1)\\
&\quad+(8-10a_1-2a_2^2+5a_1a_2)\cos(2\gamma)\Big)\\
&-\frac{1}{4}N_1N_2(4-3a_1)(2-a_1)a_1a_2\sin^2(2\gamma)\\
&+\frac{1}{24N}N_1^3a_1^3\Big(172+130a_1-108a_1^2-27a_1a_2\\
&\quad+(232-32a_1-69a_1^2+27a_1a_2)\cos(2\gamma)+15(2-a_1)^2\cos(4\gamma)\Big)\\
&-\frac{12N^{5/2}}{N_{\ 1}}N_2^{1/2}(2-a_1)(2-a_2)a_1^2r_1r_2\Big(-86-18a_1-27a_2\\
&\quad-(90-45a_1)\cos(2\gamma)\Big)\\
&+\frac{1}{24N}N_1^2N_2a_1^2a_2\Big(172-42a_1+172a_2-81a_2^2-54a_1a_2\\
&\quad+(8-48a_1-64a_2+81a_2^2-27a_1a_2)\cos(2\gamma)\\
&\quad-45(2-a_1)(2-a_2)\cos(4\gamma)\Big)\\
&+\frac{1}{4N}(N_1N_2)^{3/2}(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(10-a_2\\
&\quad-5(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&-\frac{9}{N^2}N_1^4(2-a_1)a_1^5\cos^2(\gamma)-\frac{9}{N^2}N_1^2N_2^2(2-a_2)a_1^2a_2^3\sin^2(\gamma)\\
&+\frac{1}{N^2}N_1^3N_2a_1^3a_2\Big(a_1a_2-a_1-a_2+(a_1-a_2)\cos(2\gamma)\Big)\\
&-\frac{9}{N^2}N_1^{5/2}N_2^{1/2}\bar{a}^2N(2-a_1)(2-a_2)a_1^2r_1r_2\sin(2\gamma)\Big].
\end{aligned}
\tag{F.1}
$$

$$
\begin{aligned}
\langle \hat{n}_{p1}\hat{n}_{p2}\rangle_L \;=\; & \frac{N_1N_2a_1a_2}{4}+\frac{1}{2}\Big(N_1a_1(1-a_2)\sin^2(\gamma)+N_2a_2(1-a_1)\Big)\cos^2(\gamma)\\
&+\frac{1}{4}(N_1N_2)^{1/2}(2-a_1)(2-a_2)r_1r_2\sin(2\gamma)\\
&-\frac{1}{4N}\Big[N_1N_2a_1a_2(-8+2a_1+2a_2+(a_1-a_2)\cos(2\gamma))\\
&\quad+2N_1a_1\Big(-(2-a_2)(1-a_2)+(a_1-a_2)(1-a_2)\cos(2\gamma)\Big)\sin^2(\gamma)\\
&\quad+(N_1N_2)^{1/2}(2-a_1)(2-a_2)r_1r_2\Big(2-a_1-a_2+(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+2N_2a_2\Big((2-a_1)(1-2a_1)+(a_1-a_2)(1-a_2)\cos(2\gamma)\Big)\\
&+\frac{1}{8N^2}\Big[-2N_1^2(2-a_1)(1-a_2)a_1^2\sin^2(2\gamma)\\
&\quad+2N_1^{3/2}N_2^{1/2}(2-a_1)(2-a_2)a_1r_1r_2\Big(2-2a_1-a_2\\
&\qquad+(2a_1-3a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+N_1N_2a_1a_2\Big(60-59(a_1+a_2)+18(a_1^2+a_2^2)+12a_1a_2\\
&\qquad+6(-a_1(2-a_1)+a_2(2-a_2))\cos(2\gamma)\\
&\qquad+(4-a_1-a_2-2(a_1^2+a_2^2)+4a_1a_2)\cos(4\gamma)\\
&\quad+2N_1^{1/2}N_2^{3/2}(2-a_1)(2-a_2)a_2r_1r_2\Big(2-a_1-2_a^2+(3a_1-2a_2)\cos(2\gamma)\Big)\\
&\quad-2N_2^2(1-a_1)(2-a_2)a_2^2\sin^2(2\gamma)\Big]\\
&+\frac{1}{8N^3}\Big[2N_1^{5/2}N_2^{1/2}(2-a_1)(2-a_2)a_1^2r_1r_2\Big(2+a_1-(2-a_1)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+N_1^2N_2a_1^2a_2\Big(-8+74a_1+2a_2-27a_1^2-15a_1a_2\\
&\qquad+2(-8+16a_1+4a_2-11a_1^2+3a_1a_2)\cos(2\gamma)\\
&\qquad-(2-a_1)(4+a_1-3a_2)\cos(4\gamma)\Big)\\
&\quad2(N_1N_2)^{3/2}(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(4-9(a_1+a_2)\\
&\qquad+3(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad N_1N_2^2a_1a_2^2\Big(-8+2a_1+74a_2-27a_2^2-15a_1a_2\\
&\qquad+2(8-4a_1-16a_2+11a_2^2-3a_1a_2)\cos(2\gamma)\\
&\qquad-(2-a_2)(4-3a_1+a_2)\cos(4\gamma)\Big)\\
&\quad+2N_1^{1/2}N_2^{5/2}(2-a_1)(2-a_2)a_2^2r_1r_2\Big(2+a_2+(2-a_2)\cos(2\gamma)\Big)\Big]
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{3}{N^4}\Big[N_1^3N_2(2-a_1)a_1^4a_2\cos^2(\gamma)+N_1N_2^3(2-a_2)a_1a_2^4\sin^2(\gamma)\\
&\quad N_1^{3/2}N_2^{3/2}\bar{a^2}N(2-a_1)(2-a_2)a_1a_2r_1r_2\sin(2\gamma)\\
&\quad +(N_1N_2a_1a_2)^2\Big(a_1+a_2-a_1a_2-(a_1-a_2)\cos(2\gamma)\Big)\Big]\\
&+\frac{\bar{L}}{4N}\Big\{N_1^{1/2}N_2^{1/2}(2-a_1)(2-a_2)r_1r_2\sin(2\gamma)\\
&\quad +\frac{1}{N}\Big[N_1N_2a_1a_2(8-2a_1-2a_2+(a_1-a_2)\cos(2\gamma))\\
&\quad +2N_1a_1\Big((2-a_2)(1-2a_2)+(1-a_2)(a_1-a_2)\cos(2\gamma)\Big)\sin^2(\gamma)\\
&\quad +(N_1N_2)^{1/2}(2-a_1)(2-a_2)r_1r_2\Big(2-a_1-a_2\\
&\qquad +(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +2N_2a_2\Big((2-a_1)(1-2a_1)+(1-a_1)(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&\quad +\frac{1}{N^2}\Big[2N_1^2(2-a_1)(1-a_2)a_1^2\sin^2(2\gamma)+2N_2^2(1-a_1)(2-a_2)a_2^2\sin^2(2\gamma)\\
&\quad -2N_1^{3/2}N_2^{1/2}(2-a_1)(2-a_2)a_1r_1r_2\Big(1-2a_1-a_2\\
&\qquad +(2a_1-3a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +N_1N_2a_1a_2\Big(2(-19+26(a_1+a_2)-9(a_1+a_2^2)-6a_1a_2)\\
&\qquad +(19(a_1-a_2)-12(a_1^2-a_2^2))\cos(2\gamma)\\
&\qquad +(-4+a_1+a_2+2(a_1^2+a_2^2)-4a_1a_2)\cos(4\gamma)\Big)\\
&\quad -N_1^{1/2}N_2^{3/2}(2-a_1)(2-a_2)a_2r_1r_2\Big(1-a_1-2a_2\\
&\qquad +(3a_1-2a_2)\cos(2\gamma)\Big)\Big]\\
&\quad +\frac{3}{2N^3}\Big[-2N_1^{5/2}N_2^{1/2}(2-a_1)(2-a_2)a_1^2r_1r_2\Big(2+a_1\\
&\qquad +(2-a_1)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +N_1^2N_2a_1^2a_2\Big(-70a_1-2a_2+27a_1^2+15a_1a_2\\
&\qquad +2(4-14a_1-4a_2+11a_1^2-3a_1a_2)\cos(2\gamma)\\
&\qquad +2(2-a_1)(4+a_1-3a_2)\cos(4\gamma)\Big)\\
&\quad +6(N_1N_2)^{3/2}(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(-3(a_1+a_2)\\
&\qquad +(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&+N_1N_2^2a_1a_2^2\Big(-2a_1-70a_2+27a_2^2+15a_1a_2\\
&\quad+2(-4+4a_1+14a_2-11a_2^2+3a_1a_2)\cos(2\gamma)\\
&\quad+2(2-a_2)(4-3a_1+a_2)\cos(4\gamma)\Big)\\
&+2N_1^{1/2}N_2^{5/2}(2-a_1)(2-a_2)a_2^2r_1r_2\Big(-(2+a_2)\\
&\quad+(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&+\frac{12}{N^4}\Big[N_1^3N_2(2-a_1)a_1^4a_2\cos^2(\gamma)+N_1N_2^3(2-a_2)a_1a_2^4\sin^2(\gamma)\\
&\quad+(N_1N_2a_1a_2)^2\Big(a_1+a_2-a_1a_2-(a_1-a_2)\cos(2\gamma)\Big)\\
&\quad+(N_1N_2)^{3/2}\bar{a}^2N(2-a_1)(2-a_2)a_1a_2r_1r_2\sin(2\gamma)\Big]\Big\}\\
&+\frac{\bar{L}^2}{48N^4}\Big\{-6N_1^2(2-a_1)(1-a_2)a_1^2\sin^2(2\gamma)\\
&\quad+6N_1^{3/2}N_2^{1/2}(2-a_1)(2-a_2)a_1r_1r_2\Big(-2-a_1+(3a_1-4a_2)\cos(2\gamma)\Big)\\
&\quad+N_1N_2a_1a_2\Big(-68-53(a_1+a_2)+39(a_1^2+a_2^2)+18a_1a_2\\
&\quad\quad+2(14(a_1-a_2)+9(a_1^2-a_2^2))\cos(2\gamma)\\
&\quad\quad+3(4-a_1-a_2-3(a_1^2+a_2^2)+6a_1a_2)\cos(4\gamma)\Big)\\
&\quad-6N_1^{1/2}N_2^{3/2}(2-a_1)(2-a_2)a_2r_1r_2\Big(2+a_2\\
&\quad\quad-(4a_1-3a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad-6N_2^2(1-a_1)(2-a_2)a_2^2\sin^2(2\gamma)\\
&+\frac{1}{N}\Big[6N_1^{5/2}N_2^{1/2}(2-a_1)(2-a_2)a_1^2r_1r_2\Big(10-a_1\\
&\quad\quad+5(2-a_1)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+N_1^2N_2a_1^2a_2\Big(344+302a_1-42a_2-189a_1^2-81a_1a_2\\
&\quad\quad+2(112+16a_1+24a_2-75a_1^2+27a_1a_2)\cos(2\gamma)\\
&\quad\quad-15(2-a_1)(4+a_1-3a_2)\cos(4\gamma)\Big)\\
&\quad+2(N_1N_2)^{3/2}(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(172+45(a_1+a_2)\\
&\quad\quad-45(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+N_1N_2^2a_1a_2^2\Big(344-42a_1+302a_2-189a_2^2-81a_1a_2\\
&\quad\quad+2(-112-24a_1-16a_2+75a_2^2-27a_1a_2)\cos(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&\quad -15(2-a_2)(4-3a_1+a_2)\cos(4\gamma)\Big)\\
&+6N_1^{1/2}N_2^{5/2}(2-a_1)(2-a_2)a_2^2r_1r_2\Big(10-a_2\\
&\quad -5(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&-\frac{432}{N^2}\Big[N_1^3N_2(2-a_1)a_1^4a_2\cos^2(\gamma)+N_1N_2^3(2-a_2)a_1a_2^4\sin^2(\gamma)\\
&+(N_1N_2a_1a_2)^2\Big(a_1+a_2-a_1a_2-(a_1-a_2)\cos(2\gamma)\Big)\\
&+(N_1N_2)^{3/2}\bar{a}^2N(2-a_1)(2-a_2)a_1a_2r_1r_2\sin(2\gamma)\Big]\Big\}. \qquad \text{(F.2)}
\end{aligned}
$$

$$
\begin{aligned}
\langle\hat{D}_1\cdot D_1\rangle_{LA} &= N_1^2(2-a_1)a_1\\
&+N_1\Big((1-4a_1)(4-a_1)-(1-6a_1+3a_1^2)\cos(2\gamma)\Big)\\
&+\frac{N_1^2}{N}(2-a_1)a_1(-3+4a_1+2(1-a_1)\cos(2\gamma))\\
&-\frac{N_1^{3/2}N_2^{1/2}}{N}2(2-a_1)(1-a_1)(2-a_2)r_1r_2\sin(2\gamma)\\
&-(2-a_1)\left(1-3a_1+(1-3a_1)\cos(2\gamma)\right)\\
&+\frac{1}{4N}N_1\Big(2(33a_1-a_2-62a_1^2+6a_1a_2+23a_1^3-3a_1^2a_2)\\
&\qquad +2a_1(6-11a_1+4a_1^2)\cos(2\gamma)\\
&\qquad -2(1-6a_1+3a_1^2)(a_1-a_2)\cos(4\gamma)\Big)\\
&+\frac{1}{2N^2}\Big[N_1^2(2-a_1)a_1\Big(1-42a_1-8a_2+39a_1^2+6a_2^2+2a_1a_2\\
&\qquad -2(2+9a_1-5a_2-11a_1^2+3a_2^2+2a_1a_2)\cos(2\gamma)\\
&\qquad -(1-8a_1+2a_2+5a_1^2-2a_1a_2)\cos(4\gamma)\Big)\\
&\quad -2N_1^{3/2}N_2^{1/2}r_1r_2\Big(2(2-3a_1+a_1^2)(2-a_2)(1+2a_1+a_2)\\
&\qquad +(2-14a_1+a_2+8a_1^2-a_2^2+5a_1a_2-4a_1^2a_2+a_1a_2^2)\cos(2\gamma)\Big)\\
&\qquad \times\sin(2\gamma)\\
&\quad -2N_1N_2(1-6a_1+3a_1^2)(2-a_2)\sin^2(2\gamma)\Big]\\
&+\frac{1}{N^3}\Big[N_1^3(2-a_1)a_1^2\Big(2+25a_1-18a_1^2-3a_1a_2\\
&\qquad +(4+14a_1-13a_1^2+3a_1a_2)\cos(2\gamma)+(1-a_1)(2-a_1)\cos(4\gamma)\Big)\\
&\quad +2N_1^{5/2}N_2^{1/2}(2-a_1)a_1r_1r_2\Big(4+18a_1+10a_2-12a_1^2-6a_2^2-15a_1a_2
\end{aligned}
$$

$$
\begin{aligned}
&+6a_1^2a_2+3a_1a_2^2-3(2-a_1)(1-a_1)(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+N_1^2N_2(2-a_1)a_1a_2\Big(2+2a_1+23a_2-9a_2^2-12a_1a_2\\
&\quad+(4-8a_1-10a_2+9a_2^2-3a_1a_2)\cos(2\gamma)\\
&\quad-3(1-a_1)(2-a_2)\cos(4\gamma)\Big)\\
&+2(N_1N_2)^{3/2}(2-a_1)(1-a_1)(2-a_2)a_2r_1r_2\Big(2+a_2\\
&\quad-(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&+\frac{12}{N^4}(2-a_1)a_1\Big[-N_1^4(2-a_1)a_1^3\cos^2(\gamma)-N_1^2N_2^2(2-a_2)a_2^3\sin^2(\gamma)\\
&\quad+N_1^3N_2a_1a_2(a_1a_2-a_1-a_2+(a_1-a_2)\cos(2\gamma)\\
&\quad-N_1^{5/2}N_2^{1/2}\bar{a}^2N(2-a_1)(2-a_2)r_1r_2\sin(2\gamma)\Big]\\
&+\frac{\bar{L}}{N^2}\Big\{N_1^2(2-a_1)a_1(3-4a_1-2(1-a_1)\cos(2\gamma))\\
&\quad+2N_1^{3/2}N_2^{1/2}(2-a_1)(1-a_1)(2-a_2)r_1r_2\sin(2\gamma)\\
&\quad+\frac{1}{2}N_1\Big(-33a_1-a_2+62a_1^2-6a_1a_2-23a_1^3+3a_1^2a_2\\
&\quad\quad-4a_1(6-11a_1+4a_1^2)\cos(2\gamma)\\
&\quad\quad+(1-6a_1+3a_1^2)(a_1-a_2)\cos(4\gamma)\Big)\\
&\quad-(N_1N_2)^{1/2}(6-7a_1+2a_1^2)(2-a_2)r_1r_2\sin(2\gamma)\\
&\quad+\frac{1}{N}\Big[N_1^2(2-a_1)a_1\Big(11+31a_1+5a_2-39a_1^2-6a_2^2-2a_1a_2\\
&\quad\quad+(8+11a_1-7a_2-22a_1^2+6a_2^2+4a_1a_2)\cos(2\gamma)\\
&\quad\quad+(1-8a_1-2a_2-5a_1^2+2a_1a_2)\cos(4\gamma)\Big)\\
&\quad+4N_1^{3/2}N_2^{1/2}(2-a_1)r_1r_2\Big((1-a_1)(4+4a_1-a_2^2-2a_1a_2)\\
&\quad\quad+(2-14a_1+a_2+8a_1^2-a_2^2+5a_1a_2-4a_1^2a_2+a_1a_2^2)\cos(2\gamma)\Big)\\
&\quad+2N_1N_2(1-6a_1+3a_1^2(2-a_2)a_2\sin^2(2\gamma)\Big]\\
&+\frac{3}{N^2}(2-a_1)\Big[-N_1^3a_1^2\Big(6+23a_1-18a_1^2-3a_1a_2\\
&\quad\quad+(8+12a_1-13a_1^2+3a_1a_2)\cos(2\gamma)\\
&\quad\quad+(2-a_1)(1-a_1)\cos(4\gamma)\Big)\\
&\quad-2N_1^{5/2}N_2^{1/2}a_1r_1r_2\Big(12+14a_1+6a_2-12a_1^2-6a_2^2-13a_1a_2+6a_1^2a_2\\
&\quad\quad-3a_1a_2^2+3(2-a_1)(1-a_1)(2-a_2)a_1\cos(2\gamma)\Big)\sin(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&-N_1^2N_2a_1a_2\Big(6+2a_1+21a_2^2-9a_2^2-12a_1a_2-(8a_1+8a_2-9a_2^2\\
&\quad+3a_1a_2)\cos(2\gamma)-(1-a_1)(2-a_2)\cos(4\gamma)\Big)\\
&+(N_1N_2)^{3/2}(1-a_1)(2-a_2)a_2r_1r_2\Big(-2-a_2+(2-a_2)\cos(2\gamma)\Big)\\
&\quad\times\sin(2\gamma)\Big]\\
&+\frac{48}{N^3}(2-a_1)a_1\Big[N_1^4(2-a_1)a_1^3\cos^2(\gamma)+N_1^2N_2^2(2-a_2)a_2^3\sin^2(\gamma)\\
&\quad+N_1^3N_2(2-a_1)(2-a_2)a_1a_2(a_1+a_2-a_1a_2-(a_1-a_2)\cos(2\gamma))\\
&\quad+N_1^{5/2}N_2^{1/2}\bar{a^2}N(2-a_1)(2-a_2)r_1r_2\sin(2\gamma)\Big]\Big\}\\
&+\frac{\bar{L}^2}{12N^4}\Big\{-N_1^2(2-a_1)a_1\Big(125-22a_1-16a_2-87a_1^2-18a_2^2+12a_1a_2\\
&\quad+2(30-26a_1-2a_2-15a_1^2+9a_2^2)\cos(2\gamma)\\
&\quad+3(1-10a_1+4a_2+7a_1^2-4a_1a_2)\cos(4\gamma)\Big)\\
&-12N_1^{3/2}N_2^{1/2}(2-a_1)(2-a_2)r_1r_2\Big((1-a_1)(5+a_1)\\
&\quad+(1-8a_1+2a_2+5a_1^2-2a_1a_2)\cos(2\gamma)\Big)\\
&-6N_1N_2(1-6a_1+3a_1^2)(2-a_2)a_2\sin^2(2\gamma)\\
&+\frac{1}{N}\Big[+2N_1^3(2-a_1)a_1^2\Big(154+79a_1-108a_1^2-27a_1a_2+(184-32a_1\\
&\quad-69a_1^2+27a_1a_2)\cos(2\gamma)+15(1-a_1)(2-a_2)\cos(4\gamma)\Big)\\
&+4N_1^{5/2}N_2^{1/2}(2-a_1)a_1r_1r_2\Big(308-106a_1-46a_2-36a_1^2-54a_2^2-a_1a_2\\
&\quad+18a_1^2a_2+27a_1a_2^2+45(2-a_1)(1-a_1)(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+2N_1^2N_2(2-a_1)a_1a_2\Big(154-42a_1+121a_2-81a_2^2-54a_1a_2\\
&\quad+(64+48a_1+52a_2-81a_2^2+27a_1a_2)\cos(2\gamma)\\
&\quad-45(1-a_1)(2-a_2)\cos(4\gamma)\Big)\\
&+12(N_1N_2)^{3/2}(2-a_1)(1-a_1)(2-a_2)a_2r_1r_2\Big(10-a_2\\
&\quad-5(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&-\frac{384}{N^2}(2-a_1)a_1\Big[N_1^4(2-a_1)a_1^3\cos^2(\gamma)+N_1^2N_2^2(2-a_2)a_2^3\sin^2(\gamma)\\
&+N_1^3N_2a_1a_2\Big(a_1+a_2-a_1a_2-(a_1-a_2)\cos(2\gamma)\Big)\\
&+N_1^{5/2}N_2^{1/2}\bar{a^2}N(2-a_1)(2-a_2)r_1r_2\sin(2\gamma)\Big]\Big\}. \qquad \text{(F.3)}
\end{aligned}
$$

$$
\begin{aligned}
\langle \hat{D}_1 \cdot D_2 \rangle_L \;=\;& N_1 N_2 (2-a_1)(2-a_2) r_1 r_2 \\
& -2(N_1 \sin^2(\gamma) + N_2 \cos^2(\gamma))(2-a_1)(2-a_2) r_1 r_2 \\
& -(N_1 N_2)^{1/2} (1-a_1)(1-a_2) \sin(2\gamma) \\
& +\frac{N_1^{1/2} N_2^{1/2}}{N} (\bar{a^2} N - (N_1 + N_2) a_1 a_2) \sin(2\gamma) \\
& +\frac{N_1 N_2}{N} (2-a_1)(2-a_2) r_1 r_2 (-3 + 2a_1 + 2a_2 + (a_1 - a_2)\cos(2\gamma)) \\
& +\frac{2}{N} N_1 (2-a_1)(2-a_2) r_1 r_2 (1 - 2a_2 + \\
& \qquad (a_1 - a_2)\cos(2\gamma)) \sin^2(\gamma) \\
& +\frac{1}{N} (N_1 N_2)^{1/2} \Big(a_1 + a_2 - a_1^2 - a_2^2 - 3a_1 a_2 + a_1^2 a_2 + a_1 a_2^2 \\
& \qquad -(1-a_1)(1-a_2)(a_1 - a_2)\cos(2\gamma) \Big) \sin(2\gamma) \\
& +\frac{2}{N} N_2 (2-a_1)(2-a_2) r_1 r_2 (1 - 2a_1 + (a_1 - a_2)\cos(2\gamma)) \cos^2(\gamma) \\
& +\frac{1}{2N^2} \Big[2N_1^2 (2-a_1)^2 (2-a_2) a_1 r_1 r_2 \sin^2(2\gamma) \\
& -2N_1^{3/2} N_2^{1/2} (2-a_1) a_1 \Big(1 + 2a_1 - a_2^2 - 2a_1 a_2 \\
& \qquad +(1 - 2a_1 + 4a_2 - 3a_2^2 + 2a_1 a_2)\cos(2\gamma) \Big) \sin(2\gamma) \\
& +N_1 N_2 (2-a_1)(2-a_2) r_1 r_2 \Big(2 - 26a_1 - 26a_2 + 19a_1^2 + 18a_2^2 + 12a_1 a_2 \\
& \qquad +(10a_1 - 10a_2 - 11a_1^2 + 12a_2^2)\cos(2\gamma) \\
& \qquad -2(1 - a_1^2 - a_2^2 + 2a_1 a_2)\cos(4\gamma) \Big) \\
& +2N_1^{1/2} N_2^{3/2} (2-a_2) a_2 \Big(-1 - 2a_2 + a_1^2 + 2a_1 a_2 \\
& \qquad +(1 + 4a_1 - 2a_2 - 3a_1^2 + 2a_1 a_2)\cos(2\gamma) \Big) \sin(2\gamma) \\
& +N_2^2 (2-a_1)(2-a_2)^2 a_2 r_1 r_2 \sin^2(2\gamma) \Big] \\
& +\frac{1}{2N^3} \Big[2N_1^{5/2} N_2^{1/2} (2-a_1)(1-a_2) a_1^2 \Big(2 + a_1 + (2-a_1)\cos(2\gamma) \Big) \sin(2\gamma) \\
& +N_1^2 N_2 (2-a_1) a_1 r_1 r_2 \Big(8 + 96a_1 - 54a_1^2 - 2a_2^2 - 78a_1 a_2 + 27a_1^2 a_2 \\
& \qquad +15a_1 a_2^2 + 2(24a_1 + 8a_2 - 22a_1^2 - 4a_2^2 - 6a_1 a_2 + 11a_1^2 a_2 \\
& \qquad -3a_1 a_2^2)\cos(2\gamma) - (2-a_1)(2-a_2)(2 + a_1 - 3a_2)\cos(4\gamma) \Big) \\
& +2(N_1 N_2)^{3/2} a_1 a_2 \Big(8 + 28(a_1 + a_2) - 18(a_1^2 + a_2^2) - 30a_1 a_2
\end{aligned}
$$

$$
\begin{aligned}
&+9(a_1^2a_2+a_1a_2^2)-3(2-a_1)(2-a_2)(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+N_1N_2^2(2-a_1)(2-a_2)a_2r_1r_2\Big(4+2a_1+48a_2-27a_2^2-15a_1a_2\\
&\quad-2(4a_1+12a_2-11a_2^2+3a_1a_2)\cos(2\gamma)\\
&\quad-(2-a_2)(2-3a_1+a_2)\cos(4\gamma)\Big)\\
&+2N_1^{1/2}N_2^{5/2}(1-a_1)(2-a_2)a_2^2\Big(2+a_2-(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&-\frac{1}{2N^4}\Big[24N_1^3N_2(2-a_1)^2(2-a_2)a_1^3r_1r_2\cos^2(\gamma)\\
&\quad3N_1^{5/2}N_2^{3/2}(2-a_1)(2-a_2)a_1^2a_2\Big(2(1+3a_1)+(2-a_1)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+4N_1^2N_2^2(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(3+4a_1+4a_2-5a_1a_2\\
&\quad\quad-6(a_1-a_2)\cos(2\gamma)-(3-2_a1-2a_2+a_1a_2)\cos(4\gamma)\Big)\\
&\quad+24N_1^{3/2}N_2^{5/2}(2-a_1)(2-a_2)a_1a_2^3\sin(2\gamma)\\
&\quad+24N_1N_2^3(2-a_1)(2-a_2)^2a_2^3r_1r_2\sin^2(2\gamma)\Big]\\
&+\frac{\bar{L}}{N^2}\Big\{N_1^{3/2}N_2^{1/2}(2-a_1)(1-a_2)a_1\sin(2\gamma)\\
&\quad+N_1^{1/2}N_2^{3/2}(1-a_1)(2-a_2)a_2\sin(2\gamma)\\
&\quad+N_1N_2(2-a_1)(2-a_2)r_1r_2(3-2a_1-2a_2-(a_1-a_2)\cos(2\gamma))\\
&\quad-2N_1(2-a_1)(2-a_2)r_1r_2(1-2a_2+(a_1-a_2)\cos(2\gamma))\sin^2(\gamma)\\
&\quad+(N_1N_2)^{1/2}\Big((1-a_1-a_2)(a_1a_2-a_1-a_2)\\
&\quad\quad+(1-a_1)(1-a_2)(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad-2N_2(2-a_1)(2-a_2)r_1r_2\Big(1-2a_1+(a_1-a_2)\cos(2\gamma)\Big)\cos^2(\gamma)\\
&+\frac{1}{N^3}\Big[-2N_1^2(2-a_1)^2(2-a_2)a_1r_1r_2\sin^2(2\gamma)\\
&\quad+2N_1^{3/2}N_2^{1/2}(2-a_1)a_1\Big((1-a_2)(2+2a_1+a_2)\\
&\quad\quad+(1-2a_1+4a_2-3a_2^2+2a_1a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad N_1N_2(2-a_1)(2-a_2)r_1r_2\Big(10+19(a_1+a_2-a_1^2-a_2^2)-12a_1a_2\\
&\quad\quad+(5(a_1+a_2)-11(a_1^2+a_2^2))\cos(2\gamma)\\
&\quad\quad-2(1-a_1^2-a_2^2+2a_1a_2)\cos(4\gamma)\Big)\\
&\quad+2N_1^{1/2}N_2^{3/2}(2-a_2)a_2\Big((1-a_1)(2+a_1+2a_2)
\end{aligned}
$$

$$
\begin{aligned}
&\quad -(1+4a_1-2a_2-3a_1^2+2a_1a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad -2N_2^2(2-a_1)(2-a_2)^2a_2r_1r_2\sin^2(2\gamma)\Big]\\
&-\frac{1}{2N^2}\Big[6N_1^{5/2}N_2^{1/2}(2-a_1)(1-a_2)a_1^2\Big(2+a_1+(2-a_1)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +3N_1^2N_2(2-a_1)a_1r_1r_2\Big(24+88a_1-8a_2-54a_1^2-2a_2^2-74a_1a_2\\
&\qquad +27a_1^2a_2+15a_1a_2^2+2(8+20a_1+4a_2-22a_1^2-4a_2^2-4a_1a_2\\
&\qquad +11a_1^2a_2-3a_1a_2^2)\cos(2\gamma)\\
&\qquad +(2-a_1)(2-a_2)(2+a_1-3a_2)\cos(4\gamma)\Big)\\
&\quad +6(N_1N_2)^{3/2}a_1a_2\Big(24+20(a_1+a_2)-18(a_1^2+a_2^2)-26a_1a_2\\
&\qquad +9a_1a_2(a_1+a_2)-3(2-a_1)(2-a_2)(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +3N_1N_2^2(2-a_1)(2-a_2)a_2r_1r_2\Big(12+2a_1+44a_2-27a_2^2-15a_1a_2\\
&\qquad -2(4+4a_1+10a_2-11a_2^2+3a_1a_2)\cos(2\gamma)\\
&\qquad -(2-a_2)(2-3a_1+a_2)\cos(4\gamma)\Big)\\
&\quad +6N_1^{1/2}N_2^{5/2}(1-a_1)(2-a_2)a_2^2\Big(2+a_2-(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&+\frac{48}{N^3}\Big[N_1^3N_2(2-a_1)^2(2-a_2)a_1^3r_1r_2\cos^2(\gamma)\\
&\quad +N_1^{5/2}N_2^{3/2}(2-a_1)(2-a_2)a_1^3a_2\sin(2\gamma)\\
&\quad +N_1^{3/2}N_2^{5/2}(2-a_1)(2-a_2)a_1a_2^3\sin(2\gamma)\\
&\quad +N_1N_2^3(2-a_1)(2-a_2)^2a_2^3r_1r_2\sin^2(\gamma)\Big]\Big\}\\
&+\frac{\bar{L}^2}{12N^4}\Big\{6N_1^2(2-a_1)^2(2-a_2)a_1r_1r_2\sin^2(2\gamma)\\
&\quad -N_1^{3/2}N_2^{1/2}(2-a_1)a_1\Big((5-2a_1)(1-a_2)\\
&\qquad +(1-3a_1+5a_2-4a_2^2+3a_1a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad -N_1N_2(2-a_1)(2-a_2)r_1r_2\Big(2(-61+8(a_1+a_2)+21(a_1^2+a_2^2)+9a_1a_2)\\
&\qquad +5(8(a_1-a_2)+3(a_1^2-a_2^2))\cos(2\gamma)\\
&\qquad +3(2-3(a_1^2+a_2^2)+6a_1a_2)\cos(4\gamma)\Big)\\
&\quad -N_1^{1/2}N_2^{3/2}(2-a_2)a_2\Big(6(5-2a_2)\\
&\qquad -(1+5a_1-3a_2-4a_1^2+3a_1a_2)\cos(2\gamma)\Big)\sin(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&+6N_2^2(2-a_1)(2-a_2)^2a_2r_1r_2\sin^2(2\gamma)\\
&+\frac{1}{12N}\Big[6N_1^{5/2}N_2^{1/2}(2-a_1)(1-a_2)a_1^2\Big(10-a_1+5(2-a_1)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+N_1^2N_2(2-a_1)a_1r_1r_2\Big(616+400a_1-392a_2-378a_1^2+42a_2^2-363a_1a_2\\
&\qquad+189a_1^2a_2+81a_1a_2^2+2(247+20a_1-76a_2-150a_1^2-24a_2^2\\
&\qquad+44a_1a_2+75a_1^2a_2-27a_1a_2^2)\cos(2\gamma)\\
&\qquad+15(2-a_1)(2-a_2)(2+a_1-3a_2)\cos(4\gamma)\Big)\\
&\quad+2(N_1N_2)^{1/2}a_1a_2\Big(616-152(a_1+a_2)-90(a_1^2+a_2^2)-2a_1a_2\\
&\qquad+45a_1a_2(a_1+a_2)-45(2-a_1)(2-a_2)(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+N_1N_2^2(2-a_1)(2-a_2)a_2r_1r_2\Big(308-42a_1+200a_2-189a_2^2-81a_1a_2\\
&\qquad-2(124+24a_1+10a_2-75a_2^2+27a_1a_2)\cos(2\gamma)\\
&\qquad-15(2-a_2)(2-3a_1+a_2)\cos(4\gamma)\Big)\\
&\quad+6N_1^{1/2}N_2^{5/2}(1-a_1)(2-a_2)a_2^2\Big(10-a_2-5(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&-\frac{36}{N^2}\Big[N_1^3N_2(2-a_1)^2(2-a_2)a_1^3r_1r_2\cos^2(\gamma)\\
&\quad+N_1^{5/2}N_2^{3/2}(2-a_1)(2-a_2)a_1^3a_2\sin(2\gamma)\\
&\quad+N_1^{3/2}N_2^{5/2}(2-a_1)(2-a_2)a_1a_2^3\sin(2\gamma)\\
&\quad+N_1N_2^3(2-a_1)(2-a_2)^2a_2^3r_1r_2\sin^2(\gamma)\Big]\Big\}. \qquad \text{(F.4)}
\end{aligned}
$$

$$
\begin{aligned}
\langle M_4\rangle_L \;=\;& \frac{1}{4}N_1N_2(2-a_1)(2-a_2)(r_1-r_2)^2\sin(2\gamma)\\
&+\frac{1}{4}(N_1\sin^2(\gamma)+N_2\cos^2(\gamma))(2-a_1)(2-a_2)(1+r_1-r_2+r_1r_2)\\
&\quad\times(1-r_1+r_2+r_1r_2)\\
&-\frac{1}{4}(N_1N_2)^{1/2}(2-a_1)(2-a_2)(1+r_1r_2)^2\sin(2\gamma)\\
&+\frac{1}{4N}N_1^{3/2}N_2^{1/2}(2-a_1)(a_1(2-a_1-a_1a_2)\\
&\quad-2r_1r_2(2-a_1)(2-a_2)(1-a_1))\sin(2\gamma)\\
&+\frac{1}{2N}N_1N_2(a_1+a_2-2)(2(a_1+a_2-a_1a_2)+(a_1-a_2)\cos(2\gamma))\\
&-\frac{1}{4N}N_1^{1/2}N_2^{3/2}(2-a_2)(a_2(2-a_2-a_1a_2)\\
&\quad-2r_1r_2(2-a_1)(2-a_2)(1-a_2))\sin(2\gamma)\\
&+\frac{1}{2N}(N_1\sin^2(\gamma)+N_2\cos^2(\gamma))(a_2-a_1)(2-a_1-a_2+a_1a_2)\cos(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{1}{4N}(N_1N_2)^{1/2}\Big(a_1a_2(4-a_1-a_2)+(2(a_1-a_2)-a_1^2+a_2^2+a_1^2a_2-a_1a_2^2)\\
&\qquad\times\cos(2\gamma)\Big)\sin(2\gamma)\\
&+\frac{1}{8N^2}\Big[-2N_1^2(2-a_1)a_1(2-a_1-a_2+a_1a_2)\sin^2(\gamma)\\
&\quad+2N_1^{3/2}N_2^{1/2}(2-a_1)a_1\Big(4-2a_1-a_2^2-a_1a_2\\
&\qquad-(4-2a_1-6a_2-5a_2^2-3a_1a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+N_1N_2\Big(a_1a_2(28-17(a_1+a_2)+4a_1a_2+(a_1^2+a_b^2))-3(2-a_1)^2a_2\\
&\qquad-3(2-a_2)^2a_2+(a_1a_2(3(a_2-a_1)+a_1^2-a_2^2)-a_1(2-a_1)^2\\
&\qquad-a_2(2-a_2)^2)\cos(2\gamma)-(a_1a_2(12-5(a_1+a_2)-a_1^2-a_2^2+4a_1a_2)\\
&\qquad+a_1(2-a_1)^2+a_2(2-a_2)^2)\cos(4\gamma)\Big)\\
&\quad+2N_1^{1/2}N_2^{3/2}(2-a_2)a_2\Big(4-a_1^2-2a_2-a_1a_2\\
&\qquad-(4+6a_1-2a_2-5a_1^2+3a_1a_2)\cos(2\gamma)\Big)\\
&\quad-2N_2^2(2-a_2)a_2(2-a_1-a_2+a_1a_2)\sin^2(2\gamma)\Big]\\
&+\frac{1}{4N^3}\Big[+N_1^{5/2}N_2^{1/2}(2-a_1)a_1^2a_2(2+a_1(1-a_2)+(2-a_1)\cos(2\gamma))\sin(2\gamma)\\
&\quad+2N_1^2N_2(2-a_1)^2(2-a_2)a_1a_2\sin^2(2\gamma)\\
&\quad+(N_1N_2)^{3/2}a_1a_2\Big(32-76(a_1+a_2)+34(a_1+a_2)^2-17a_1a_2(a_1+a_2)\\
&\qquad+5(2-a_1)(2-a_2)(a_1-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+2N_1N_2^2(2-a_1)(2-a_2)^2a_1a_2\sin^2(2\gamma)\\
&\quad+N_1^{1/2}N_2^{5/2}(2-a_2)a_1a_2^2(2+a_2+(2-a_2)\cos(2\gamma))\sin(2\gamma)\Big]\\
&-\frac{1}{2N^4}\Big[24N_1^3N_2(2-a_1)^2(2-a_2)a_1^3r_1r_2\cos^2(\gamma)\\
&\quad+3N_1^{5/2}N_2^{3/2}(2-a_2)a_1^2a_2\Big(2(2+5a_1-3a_1^2)+(2-a_1)^2\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad+4N_1^2N_2^2(2-a_1)(2-a_2)a_1a_2r_1r_2\Big(3+4(a_1+a_2)+5a_1a_2\\
&\qquad-6(a_1-a_2)\cos(2\gamma)-(3-2(a_1+a_2)+a_1a_2)\cos(4\gamma)\Big)\\
&\quad+24N_1^{3/2}N_2^{5/2}(2-a_1)(2-a_2)^2a_1a_2^3\sin(2\gamma)\\
&\quad+24N_1N_2^3(2-a_1)(2-a_2)^2a_2^3r_1r_2\sin^2(\gamma)\Big]\\
&+\frac{\bar{L}}{4N^2}\Big\{2N_1^{3/2}N_2^{1/2}a_1a_2(N_1(2-a_1)+N_2(2-a_2))\sin(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&+2N_1N_2(a_1+a_2-2)(2(a_1+a_2-a_1a_2)+(a_1-a_2)\cos(2\gamma))\\
&-2(N_1\sin^2(\gamma)+N_2\cos^2(\gamma))(2(a_1-a_2)-a_1^2+a_2^2+a_1a_2(a_1-a_2))\\
&\qquad\times\cos(2\gamma)\sin^2(\gamma)\\
&+(N_1N_2)^{1/2}\Big((4-a_1-a_2)a_1a_2+2(2(a_1-a_2)-a_1^2+a_2^2+a_1a_2(a_1-a_2))\\
&\qquad\times\cos(2\gamma)\Big)\sin(2\gamma)\\
+\frac{1}{N}\Big[&2N_1^2(2-a_1)a_2(2-a_1-a_2+a_1a_2)\sin^2(2\gamma)\\
&+2N_1^{3/2}N_2^{1/2}(2-a_1)a_1\Big(-4+2a_1+17a_2-7a_2^2-3a_1a_2+2a_1a_2^2\\
&\qquad-(4-2a_1+6a_2+3a_1a_2-5a_2^2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+N_1N_2\Big(12(a_1+a_2-a_1^2-a_2^2)-28a_1a_2+17a_1a_2(a_1+a_2)\\
&\qquad+3(a_1^3+a_2^3-a_1^3a_2-a_1a_2^3)+4a_1^2a_2^2+4(4(a_1-a_2-a_1^2+a_2^2)\\
&\qquad+3a_1a_2(a_1-a_2)+a_1^3-a_2^3-a_1^3a_2+a_1a_2^3)\cos(2\gamma)+(4(a_1+a_2-a_1^2\\
&\qquad-a_2^2+a_1^2a_2^2+3a_1a_2)+a_1^3+a_2^3-a_1a_2(5a_1+5a_2-a_1^2-a_2^2))\cos(4\gamma)\Big)\\
&+2N_1^{1/2}N_2^{3/2}(2-a_2)a_2\Big(-4+17a_1+2a_2-7a_1^2-3a_1a_2+2a_1^2a_2\\
&\qquad+(4+6a_1-2a_2-5a_1^2+3a_1a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+2N_2^2(2-a_2)a_2(2-a_1-a_2+a_1a_2)\sin^2(2\gamma)\Big]\\
+\frac{1}{N^2}\Big[&3N_1^{5/2}N_2^{1/2}(2-a_1)a_1^2a_2(2+a_1-(2-a_1)\cos(2\gamma))\sin(2\gamma)\\
&-6N_1^2N_2(2-a_1)^2(2-a_2)a_1a_2\sin^2(2\gamma)\\
&+(N_1N_2)^{3/2}a_1a_2\Big(224-468(a_1+a_2)+286(a_1^2+a_2^2)+504a_1a_2\\
&\qquad-60(a_1^3+a_2^3)-203a_1a_2(a_1+a_2)+30a_1a_2(a_1^2+a_2^2+a_1a_2)\\
&\qquad+3(a_1-a_2)(2-a_1)(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&-6N_1N_2^2(2-a_1)(2-a_2)^2a_1a_2\sin^2(2\gamma)\\
&+N_1^{1/2}N_2^{5/2}(2-a_2)a_1a_2^2(2+a_2+(2-a_2)\cos(2\gamma))\sin(2\gamma)\Big]\\
+\frac{2}{N^3}\Big[&6N_1^3N_2(2-a_1)^2(2-a_2)a_1^3a_2(r_1-r_2)^2\cos^2(\gamma)\\
&+N_1^{5/2}N_2^{3/2}(2-a_1)^2(2-a_2)^2a_1r_1(r_1-r_2)^2\Big(2r_1(2+4a_1-a_2-2a_1a_2)\\
&\qquad-2r_2(1+2a_1)+r_1(4-2a_1-2a_2+a_1a_2)\cos(2\gamma)\\
&\qquad-r_2(2-a_1)\cos(2\gamma)\Big]\sin(2\gamma)
\end{aligned}
$$

$$
\begin{aligned}
&+N_1^{3/2}N_2^{5/2}(2-a_1)^2(2-a_2)^2a_2r_1(r_1-r_2)^2\Big(2r_1(2+3a_2-2a_2^2)\\
&\quad -2r_2(1+a_2)-r_1(4-4a_2+a_2^2)\cos(2\gamma)+r_2(2-a_2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&+6N_1N_2^3(2-a_1)(2-a_2)^2a_2^3(r_1-r_2)^2\sin^2(\gamma)\Big]\Big\}\\
&+\frac{\bar{L}^2}{12N^4}\Big\{6N_1^2(2-a_1)^2(2-a_2)a_1r_1r_2\sin^2(2\gamma)\\
&\quad -6N_1^{3/2}N_2^{1/2}(2-a_1)a_1\Big((5+a_1)(1-a_2)\\
&\quad +(1-3a_1+5a_2+3a_1a_2-4a_2^2)\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +N_1N_2(2-a_1)(2-a_2)r_1r_2\Big(122-16(a_1+a_2)-42(a_1^2+a_2^2)-18a_1a_2\\
&\quad -(40(a_1+a_2)-15(a_1^2+a_2^2))\cos(2\gamma)-(6+9(a_1+a_2)^2)\cos(4\gamma)\Big)\\
&\quad -6N_1^{1/2}N_2^{3/2}(2-a_2)a_2\Big((5+a_2)(1-a_1)+(1+5a_1-3a_2-4a_1^2+3a_1a_2)\\
&\quad \times\cos(2\gamma)\Big)\\
&\quad +6N_2^2(2-a_1)(2-a_2)^2a_2r_1r_2\sin^2(2\gamma)\\
&+\frac{1}{N}\Big[+6N_1^{5/2}N_2^{1/2}(1-a_2)a_1^2\Big(20-12a_1+a_1^2+5(2-a_1)^2\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +N_1^2N_2(2-a_1)a_1\Big(+308+200a_1-42a_2-189a_1^2+27a_1a_2\\
&\quad +2(124+10a_1+24a_2-75a_1^2+27a_1a_2)\cos(2\gamma)\\
&\quad -15(2-a_1)(2-a_2)(2+a_1-3a_2)\cos(4\gamma)\Big)\\
&\quad +2(N_1N_2)^{3/2}a_1a_2\Big(616-152(a_1+a_2)-90(a_1^2+a_2^2)-2a_1a_2\\
&\quad +45a_1a_2(a_1+a_2)-45(2-a_1)(2-a_2)(a_1-a_2)a_1a_2\cos(2\gamma)\Big)\sin(2\gamma)\\
&\quad +N_1N_2^2(2-a_1)(2-a_2)a_2r_1r_2\Big(308-42a_1+200a_2-189a_2^2+200a_2\\
&\quad -2(124+24a_1+10a_2-75a_2^2+27a_1a_2)\cos(2\gamma)\\
&\quad -15(2-a_1)(2-a_2)(2-3a_1+a_2)\cos(4\gamma)\Big)\\
&\quad +6N_1^{1/2}N_2^{5/2}(1-a_1)a2^2\Big(20-12a_2+a_2^2-5(2-a_2)^2\cos(2\gamma)\Big)\sin(2\gamma)\Big]\\
&-\frac{36}{N^2}\Big[N_1^3N_2(2-a_1)^2(2-a_2)a_1^3r_1r_2\cos^2(\gamma)\\
&\quad +N_1^{1/2}N_2^{1/2}(N_1^2a_1^2+a_2^2N_2^2)(2-a_1)(2-a_2)a_1a_2\sin(2\gamma)\\
&\quad +N_1N_2^3(2-a_1)(2-a_2)^2a_2^3r_1r_2\sin^2(\gamma)\Big]\Big\}. \qquad \text{(F.5)}
\end{aligned}
$$

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